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REVIEW

Hydroamination of Conjugated Dienes Catalyzed by Transition Metal Complexes

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Abstract—The review summarizes published data on the hydroamination of 1,3-dienes with various primary and secondary amines, ammonia, and ammonium salts of mineral acids in the presence of transition metal complexes under homogeneous conditions. The effects of the nature of metal, ligand, initial diene, and amine and reaction conditions on the selectivity of hydroamination are considered, and possible reaction mechanisms are discussed.

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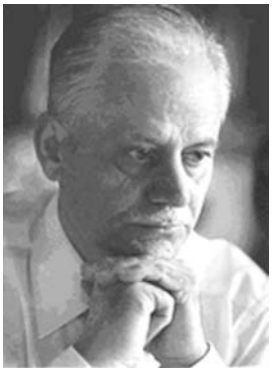
1. INTRODUCTION

Amines and their derivatives are widely used in the manufacture of medicines, chemical means for plant protection, polymeric materials, flotation agents, extractants, dyes, corrosion inhibitors, stabilizers, ion exchangers, and many other products possessing practically important properties. However, the range of commercially available amines does not always meet the existing needs, so that development of practical procedures for the preparation of new compounds is required. Large-scale procedures for the synthesis of higher amines are very limited: they include ammonolysis of aliphatic alcohols and halogen derivatives with ammonia, which leads to the formation of mixtures of higher primary, secondary, and tertiary amines. Pure primary amines are generally obtained by reduction of nitriles or nitro compounds with molecular hydrogen. These procedures cannot be used to synthesize functionally substituted and unsaturated amines with a specified structure.

Considerable progress in the synthesis of higher amines was achieved since it was found that linear dimerization of butadiene in the presence of Ni-containing catalysts and secondary amines gave a small amount of butadiene hydroamination product, 2,7-octadien-1-amine [1], together with target hydrocarbons. Apart from nickel complexes, those derived from rhodium, cobalt, platinum and palladium can be used for hydroamination of conjugated dienes, but the most efficient are nickel- and palladium-containing catalysts; they ensure selective preparation of higher amines, including functionally substituted and unsaturated derivatives [1, 2].

Catalytic hydroamination of conjugated dienes and trienes with the simplest primary and secondary amines has been discovered about 40 years ago, and vast experimental data have been accumulated since that time. Review articles on the catalytic amination have been published more than 20 years ago [3, 4].



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Fields of scientific interest: metal complex catalysis in organic and organometallic synthesis, organic chemistry of non-transition metals, chemistry of strained and cage-like compounds, chemistry of small and unstable molecules.

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Fields of scientific interest: synthetic organic chemistry, chemistry of natural and biologically active compounds, medicinal chemistry, metal complex catalysis.

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Field of scientific interest: metal complex catalysis in organic synthesis.

The existing know-how in this field, simplicity of experimental procedures for catalytic hydroamination of conjugated dienes, the possibility for synthesizing individual higher primary, secondary, and tertiary amines via a one-pot procedure, and general character make catalytic hydroamination exceptionally promising for industrial applications.

The present review was written with the goal of not only summarizing experimental data and expounding general lines in the development of studies in this field but also stimulating interest in catalytic hydroamination as a very promising field of chemistry. The review does not consider published data on the hydroamination of olefins and acetylenes; these data were discussed in recent reviews [5–10].

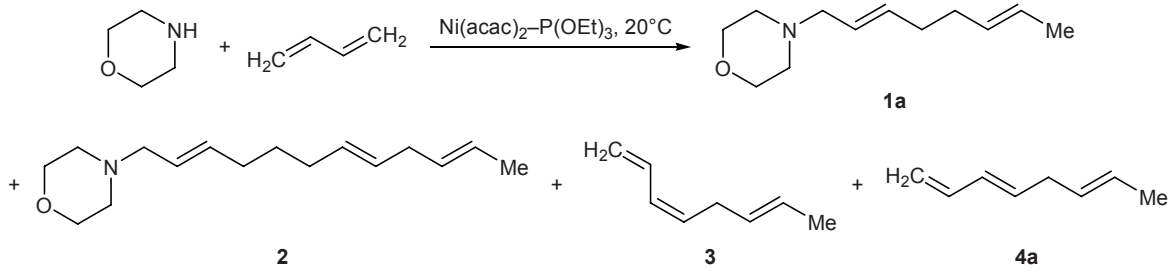
2. HYDROAMINATION OF BUTADIENE

Linear dimerization of butadiene in the presence of morpholine in the catalytic system consisting of $Ni(acac)_2$ and $P(OEt)_3$ was reported to give a small amount of 1-(octa-2,6-dien-yl)morpholine (**1a**) in addition to octa-1,3,6-trienes **3** and **4** [1] (Scheme 1). The fraction of **1a** increased to 75% when the reaction was performed at room temperature. In the absence of phosphorus-containing ligand, the product composition changed: the major products were linear dimers **3** and **4**, higher butadiene oligomers, and 1-(dodeca-2,7,10-trien-1-yl)morpholine **2** [1] (the yield of **2** was not given in [1]).

As follows from the proposed reaction scheme [1], morpholine as source of hydrogen is directly involved in the dimerization of butadiene to octa-1,3,6-trienes **3** and **4a**. A quite important step is oxidative addition of morpholine to nickel ion with cleavage of the N–H bond, which gives complex **7** (Scheme 2). The subsequent hydrogen (hydride) transfer to the activated diene molecule and coupling of the activated fragments in complex **8** yield amine **1a**. This scheme suggests that various amines can be involved in reaction with butadiene and is likely to be general for hydroamination of 1,3-dienes in the presence of transition metal complexes.

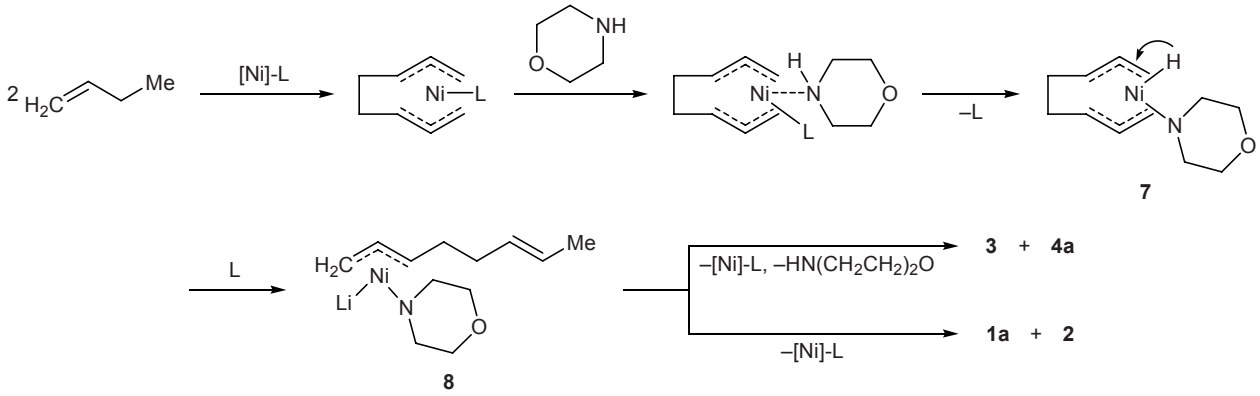
Takahashi et al. [2] reported on hydroamination of butadiene with a number of amines, such as diisopropylamine, piperidine, morpholine, butylamine, and aniline and its derivatives using palladium complexes $Pd(PPh_3)_4$ and $Pd(PPh_3)_2 \cdot C_4H_2O_3$ ($C_4H_2O_3$ is maleic anhydride). The major products were the corresponding mono- and bis(octadienyl) amines **1b** and **9**–**20** (Scheme 3).

Scheme 1.

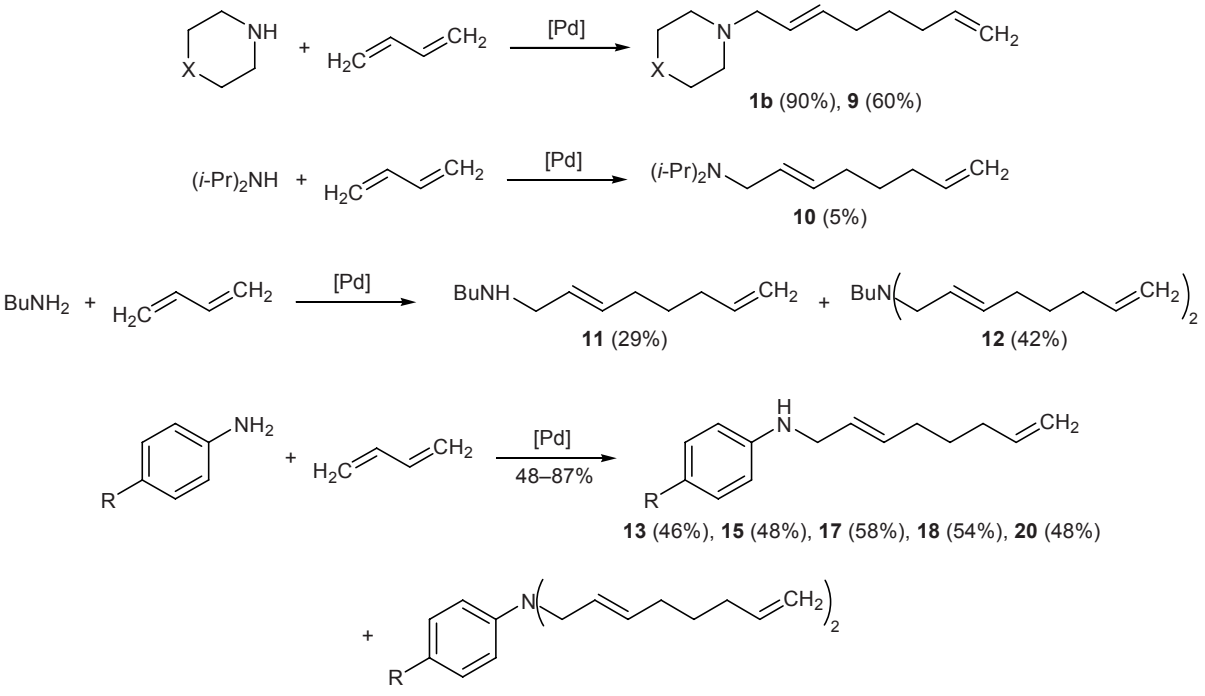


Overall yield of compounds **1**–**4** 75%; [Ni] : [L] : [morpholine] : [butadiene] = 1 : 1 : 50 : 800.

Scheme 2.

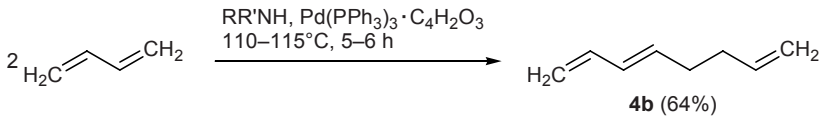


Scheme 3.



1b, X = O; **9**, X = CH_2; **13**, **14**, R = H; **15**, **16**, R = 4-Me; **17**, R = 4-Cl; **18**, **19**, R = 4-MeO; **20**, R = MeOCO; [Pd] = $Pd(PPh_3)_2 \cdot C_4H_2O_3$, 80–150°C, 0.5–8 h; solvent: initial amine or acetone.

Scheme 4.



R = H, R′ = Ac; RR′ = $(CH_2)_3C(=O)$.

It was found that, unlike coordination compounds of other metals (Ni [11–16], Rh [17–19], Pt [20–23]), palladium complexes are more efficient in the hydroamination of conjugated dienes, leading mainly to *N*-octadienyl derivatives of the corresponding amines [2, 24–31]. Butadiene failed to react with acetamide or pyrrolidinone under analogous conditions; as a result, its linear homodimerization product, octa-1,3,7-triene (**4b**) was obtained [2] (Scheme 4).

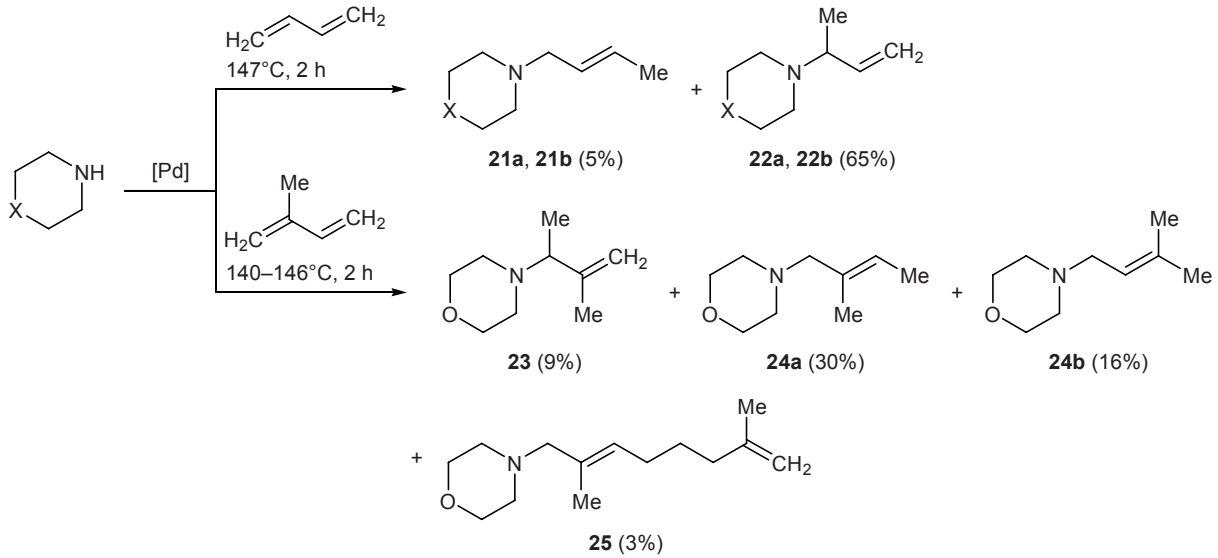
The selectivity of Pd-containing catalysts strongly depends on the initial amine structure, and it attains 90–97% for morpholine [2]. Takahashi et al. [2] tried to estimate how the basicity of the hydroaminating agent (aniline and its derivatives) is related to the overall yield and product composition in the reaction with butadiene in the presence of Pd-containing catalysts. Reduction of the amine basicity is accompanied not only by decrease in the overall yield of hydroamination products but also by complete inhibition of formation of *N*,*N*-bis(octadienyl) derivatives [2].

The effect of the amine basicity on the hydroamination of butadiene in the presence of a catalytic system consisting of $PdBr_2(Ph_2PCH_2CH_2PPh_2)_2$, PhONa, and PhOH (1 : 10 : 10) was studied in detail in [32]. It was shown that this catalytic system ensures predominant formation of 1 : 1-hydroamination products. For example, in the hydroamination of butadiene with aniline (pK_a = 4.58) and morpholine (pK_a = 8.7), the yields of 1 : 1 adducts were 67 and 79%, respectively. The overall yield of amine mixture in the reactions of butylamine (pK_a = 10.6) and piperidine (pK_a = 11.12) with butadiene did not exceed 20–30%. The authors presumed that amines with pK_a values larger than 10 form strong M–N bonds with the central metal atom of the catalyst, which hampers approach and activation of diene molecules and formation of unsaturated amines.

The corresponding 1 : 1 adducts **21** and **22** were formed as the major products (yield ~70%) in the reactions of butadiene with morpholine and piperidine, respectively, catalyzed by palladium complex with a bulky bidentate ligand, 1,2-bis(diphenylphosphino)-ethane. Likewise, isoprene reacted with morpholine in the presence of the same catalyst to produce mainly 1 : 1 adducts **23**, **24a**, and **24b**, whereas the yield of 1-(2,7-dimethylocta-2,7-dien-1-yl)morpholine (**25**, 1 : 2 adduct) did not exceed 3% [32] (Scheme 5).

Comparison of the catalytic activities of nickel and palladium complexes showed that the latter are more

Scheme 5.



[Pd] = $PdBr_2(Ph_2PCH_2CH_2PPh_2)$–NaOPh; **21**, **22**, X = O (**a**), CH_2 (**b**).

effective in the hydroamination of 1,3-dienes and that they ensure preferential formation of octadienyl derivatives [24–33]. Unlike palladium complexes, coordination compounds of nickel favor transformation of butadiene into linear and cyclic oligomers [octa-1,3,6-trienes **3** and **4a**, octa-1,3,7-triene (**4b**), 4-vinylcyclohexene (**26**), cycloocta-1,5-diene (**27**), and cyclododeca-1,5,9-triene (**28**)], and nickel-catalyzed reactions are less selective.

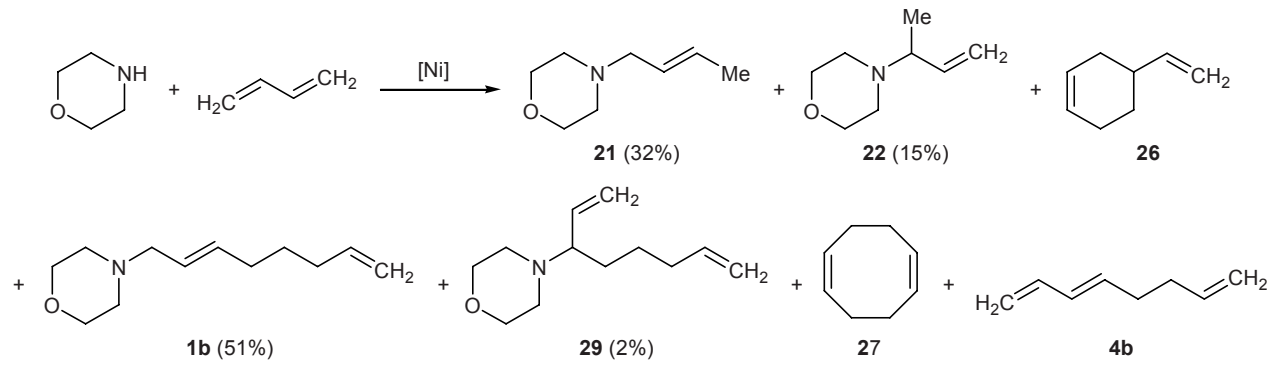
The above stated is confirmed by the results of hydroamination of butadiene with morpholine, dipropylamine, dibutylamine, and aniline using $Ni(acac)_2$–$PhP(OPr\text{-}i)_2$–$NaBH_4$ as catalytic system [14, 33]. In each case, a mixture of four unsaturated amines was obtained, and its composition depended on the initial amine. Nickel complexes favored predominant formation of 1:1 adducts (butenamines) and cyclic oligomers **26** and **28**. Morpholine reacted with butadiene in the presence of $Ni(acac)_2$–$PhP(OPr\text{-}i)_2$–$NaBH_4$ to give 1:1 adducts **21** and **22** and 1:2 adducts **1b** and **29** at a ratio of 2:1:3.4:0.1; dipropylamine was converted into butenyl and octadienyl derivatives **30**–**33** in an overall yield of 60% (0.3:6:1:2); and the overall yield of compounds **34**, **35**, and **36** obtained from butylamine was 100%. In the reactions with aniline, the fraction of butenyl derivatives **37** and **38** increased to 71%, though the overall yield decreased to 50%. The yield of isomeric octadienylamines **13** and **39** did not exceed 30% [33] (Scheme 6). Apart from unsaturated amines **1b**, **21**, **22**, and **29**, the reaction mixture contained butadiene homodimerization products (10%): octa-1,3,7-triene (**4b**), 4-vinylcyclohex-1-ene (**26**), and cycloocta-1,5-diene (**27**) at a ratio of 1:2.5:1 [33].

Somewhat surprising results were reported in [13]. It was found the two-component system $Ni(acac)_2$–$PhP(OPr\text{-}i)_2$ was more effective in the hydroamination of butadiene than the catalyst obtained by reduction of $Ni(acac)_2$ with $NaBH_4$ in the presence of $PhP(OPr\text{-}i)_2$. Presumably, this conclusion should be treated with caution, taking into account well known [34] high catalytic activity of low-valence nickel complexes stabilized by organophosphorus ligands.

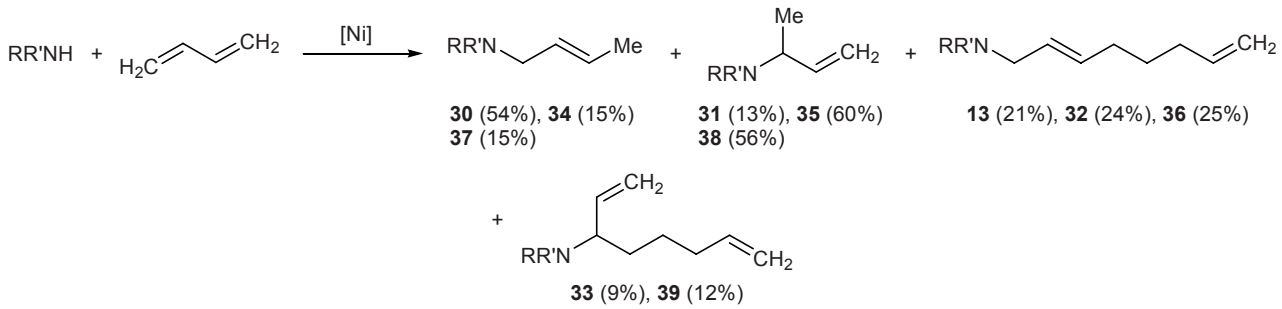
The overall yield and composition of butadiene hydroamination products with diethylamine over Ni^{2+}–$NaBH_4$–ligand strongly depended on the nature of phosphorus-containing ligand [12]. The maximal yield (67%) of a mixture of amines **40**–**43** was obtained in the presence of dialkoxy(phenyl)phosphines as ligands, the Ni–L ratio being 1:1 [12] (Scheme 7).

As shown in [20, 35, 36], hydroamination of 1,3-dienes can be catalyzed by preliminarily prepared π-allyl and π-crotyl nickel complexes activated by trialkyl

Scheme 6.

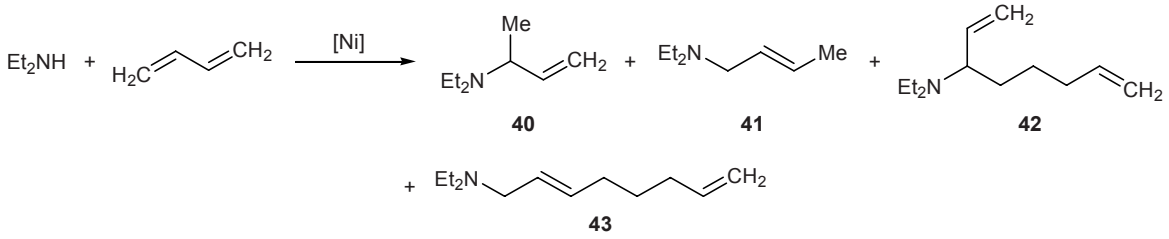


[Ni] = $Ni(acac)_2$–$PhP(OPr\text{-}i)_2$–$NaBH_4$; 100°C, 14 h.



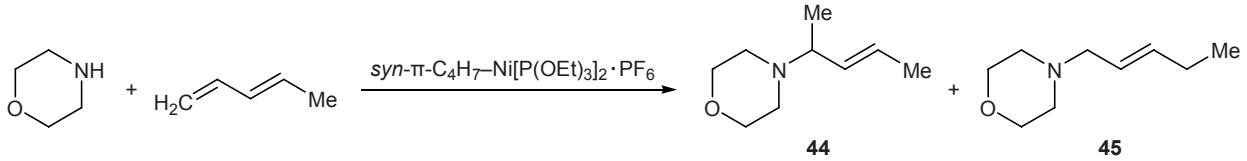
30–**33**, R = R′ = Pr; **34**–**36**, R = H, R′ = Bu; **13**, **37**–**39**, R = H, R′ = Ph.

Scheme 7.

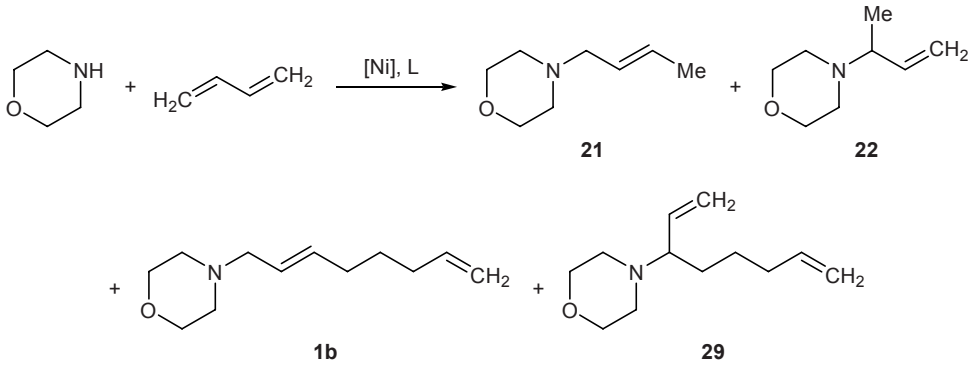


[Ni] = $Ni(acac)_2$–$PhP(OPr\text{-}i)_2$–$NaBH_4$; 90°C, 4 h;
Ni–L ratio 1 : 8: [**40**+**41**] : [**42**+**43**] = 50 : 1; Ni–L ratio 1 : 1: [**40**+**41**] : [**42**+**43**] = 1 : 50.

Scheme 8.



Scheme 9.



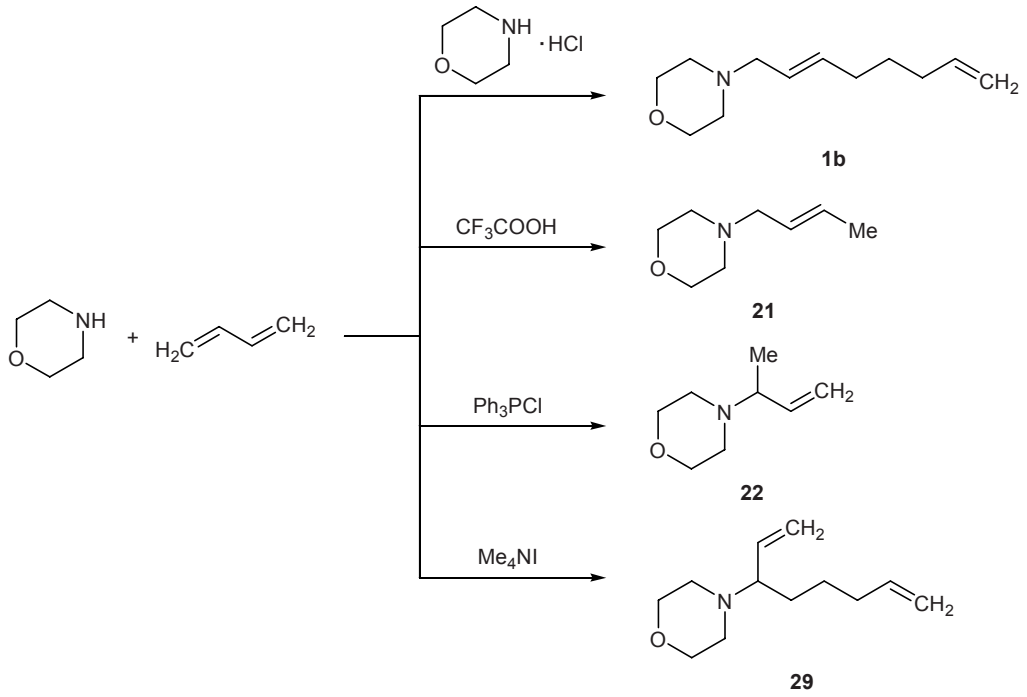
Ligand L	Overall yield	Ratio **21** : **22** : **1b** : **29**
Bu_3P	98%	31 : 1.3 : 1 : 0
$P(OEt)_3$	80%	17 : 1 : 7.5 : 0
PCl_3	64%	1 : 2.3 : 0 : 0
$P(OPh)_3$	62%	15 : 1 : 32 : 1

[Ni] = $Ni(acac)_2$–$AlEt_3$–L–CF_3COOH, 1 : 3 : 1 : 10; benzene, 80°C, 3 h.

phosphites. In particular, the complex *syn*-π-C_4H_7–$Ni[P(OEt)_3]_2 \cdot PF_6$ catalyzed the transformation of butadiene and morpholine into a mixture of isomeric amines **1a**, **21**, **22**, and **29**. In the presence of the same catalytic system, (*E*)-penta-1,3-diene reacted with morpholine to give a mixture of isomeric 1 : 1 adducts **44** and **45** in high yield (Scheme 8). Hydroamination of (*Z*)-penta-1,3-diene was characterized by very low conversion, and in both cases the major product was (*E*)-1-(pent-2-en-1-yl)morpholine (**45**).

According to the data of [37, 38], the selectivity of hydroamination of butadiene with amines can be controlled via addition of acids to the catalytic system, the best of which was found to be trifluoroacetic acid. The selectivity of hydroamination strongly depends on the concentration of CF_3CO_2H. For example, at a Ni–CF_3COOH ratio of 1 : 10, the major reaction products were 1 : 1 adducts **21** and **22**. Decrease in the trifluoroacetic acid concentration was accompanied by considerable reduction in the selectivity of hydroamination, and the products were four isomers **1b**, **21**, **22**, and **29** (Scheme 9). Addition of trifluoroacetic acid to the catalytic system made it possible to synthesize butenylamines **21** and **22** from morpholine and buta-

Scheme 10.

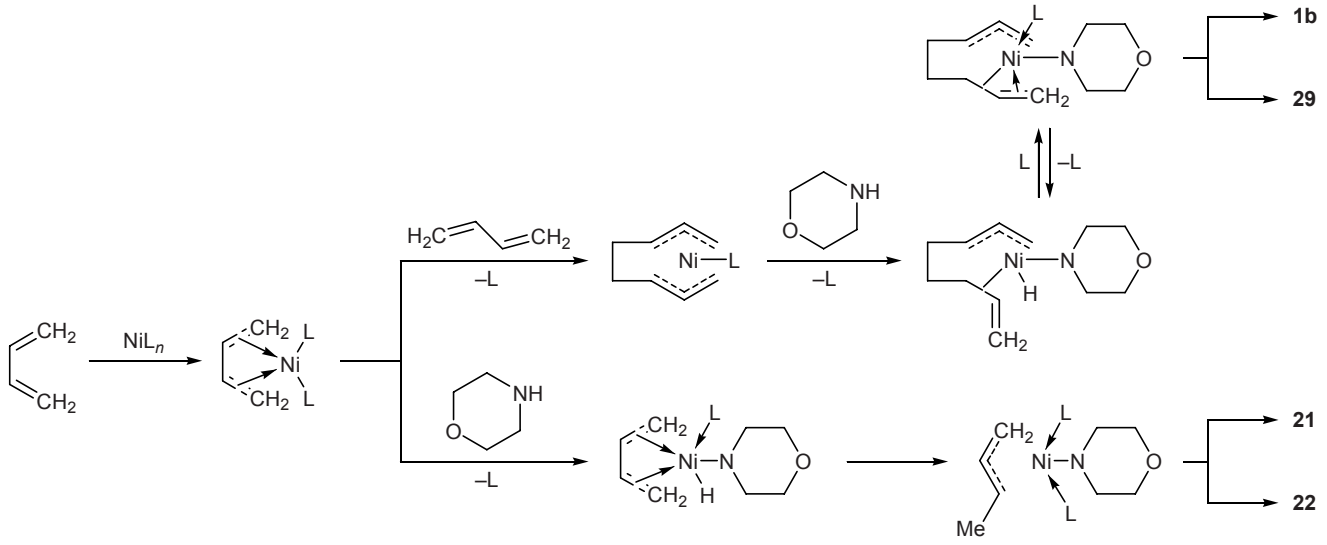


[Ni] = $Ni(acac)_2$–PBu_3–$AlEt_3$–acid; benzene, 80°C, 3 h; yield 25–98%.

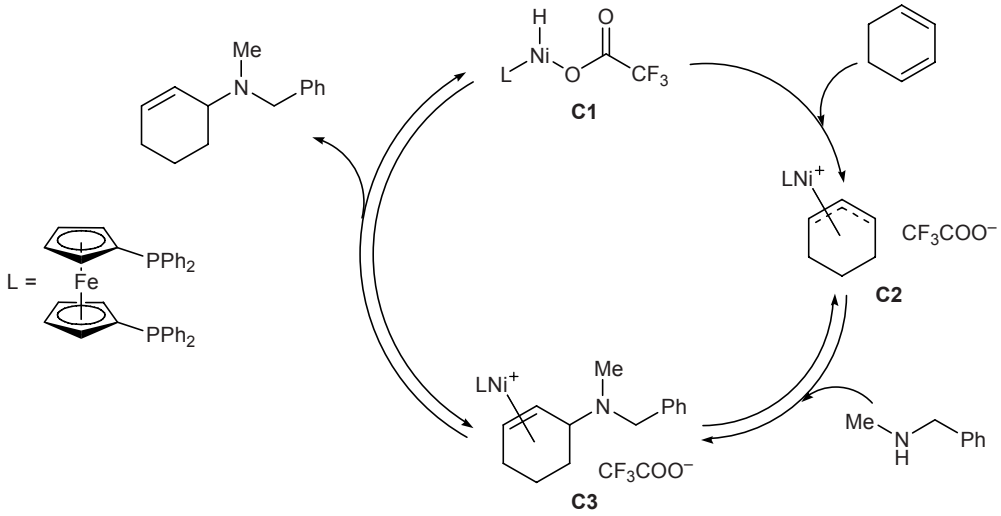
diene with almost 100% selectivity [38]. More detailed study on the reaction of morpholine with butadiene catalyzed by $Ni(acac)_2$–$AlEt_3$ showed that three- and four-component catalytic systems activated by various Lewis and Brønsted acids ensure highly selective synthesis of each of amines **1b**, **21**, **22**, and **29** [38] (Scheme 10). Scheme 11 illustrates the most probable mechanism of hydroamination of butadiene with morpholine, which rationalizes formation of not only octadienyl derivatives **1b** and **29** but also 1 : 1 adducts **21** and **22** [38, 39].

Presumably, the selectivity of hydroamination of butadiene with morpholine upon addition of trifluoroacetic acid to the catalytic system changes as a result of salt formation with the initial amine, which considerably increases lability of the N–H bond [38, 39]. The role of trifluoroacetic acid in the catalysis of hydroamination of dienes was also interpreted in terms

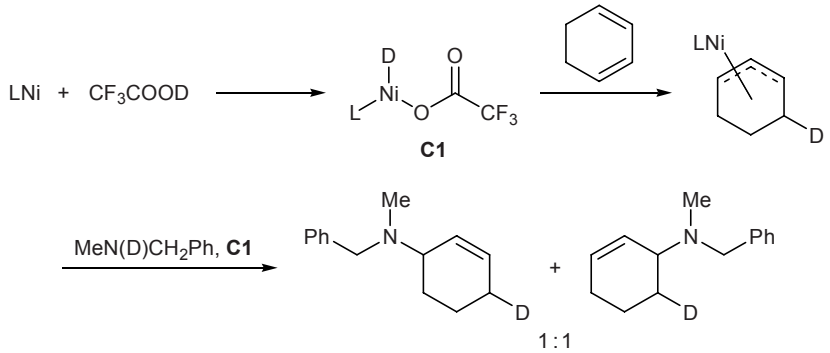
Scheme 11.



Scheme 12.



Scheme 13.

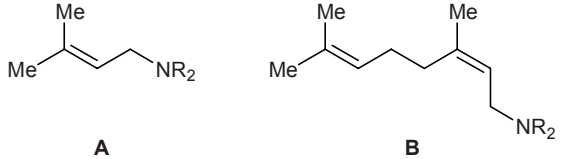


of its direct participation in the generation of nickel hydride complex **C1** [35, 40]. However, attempts to detect complex **C1** were unsuccessful because of high rate of its reaction with 1,3-diene with formation of π-allylic complex **C2** which was isolated and characterized. In the next step, attack by initial amine on π-allylic nickel complex **C2** yields π-complex **C3**, and transformation of the latter gives the final allylamine and regenerates catalytically active hydride complex **C1**, thus closing the catalytic series (Scheme 12).

The formation of π-allylic nickel complex **C2** and its participation in the catalytic hydroamination series was proved by independent experiments with deuterated *N*-methylphenylmethanamine [40] (Scheme 13).

3. HYDROAMINATION OF ISOPRENE

Hydroamination of isoprene catalyzed by palladium and nickel complexes provides a simple and convenient synthetic route to acyclic aminoterpenes [32, 41–50]. Insofar as two isoprene molecules may be coupled in four ways (head-to-tail, tail-to-head, head-to-head, and tail-to-tail), the composition of 2 : 1 adducts of isoprene and amines is usually fairly complex. Even more complex pattern may be expected for reactions of isoprene with amines and ammonia (4 : 1 adducts with amines RNH_2 and 6 : 1 adducts with NH_3, as well as *Z* and *E* isomers). From the synthetic viewpoint, the value of the procedure for the preparation of amino-substituted hemiterpenes and monoterpenes via hydroamination of isoprene is determined by its selectivity, i.e., by the ability of catalyst to ensure formation of particular isomers such as 3-methylbut-2-en-1-amine (**A**, prenylamine) and 3,7-dimethylocta-2,7-dien-1-amine (**B**). These compounds are structural elements of a diversity of natural (regular) isoprenoids [51, 52].



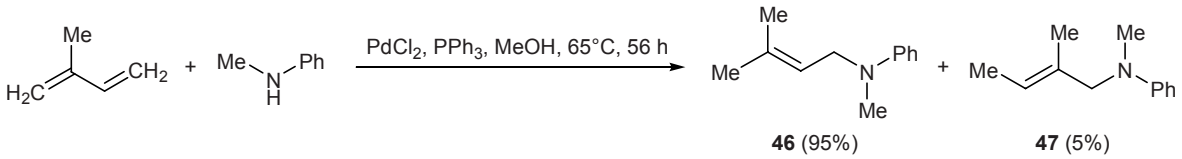
The main factors determining the regioselectivity in the reactions of isoprene with amines are (1) nature of initial amine, (2) structure of activating ligand in the catalyst, and (3) the presence of acid co-catalyst (CF_3COOH or $BF_3 \cdot Et_2O$) [43]. Solvent nature and reaction conditions are less important. 1 : 1 Adduct **46** was obtained from isoprene and *N*-methylaniline with 95% selectivity in methanol using $PdCl_2$–PPh_3 as catalyst (the overall yield of compounds **46** and **47** was 58%) [47] (Scheme 14).

Isoprene reacted with diethylamine in the presence of palladium catalyst activated by tris(2,4,6-trimethoxyphenyl)phosphine (this ligand has the largest size in the series of organophosphorus ligands; cone angle 185°) to give 2 : 1 head-to-head adduct **48** in almost quantitative yield [46] (Scheme 15).

The regioselectivity in the assembly of aminoterpenes from isoprene and diethylamine in the presence of $Pd(acac)_2$–L–acid strongly depended on the added acid; as the latter, mild and strong acids were used (CO_2, CF_3COOH, $BF_3 \cdot Et_2O$). In the absence of acid, the major product was tail-to-tail adduct **49a**, while in the presence of weak acid (CO_2) head-to-tail and tail-to-head adducts **50** and **51** were mainly formed (Scheme 16). Raising the concentration of acid and its strength favored formation of head-to-head isomer. In particular, the reaction catalyzed by Pd complex in the presence of a strong Lewis acid ($BF_3 \cdot Et_2O$) and tris(cyclohexyl)phosphine as activating ligand gave head-to-head adduct **48** with a selectivity of up to 82% [43].

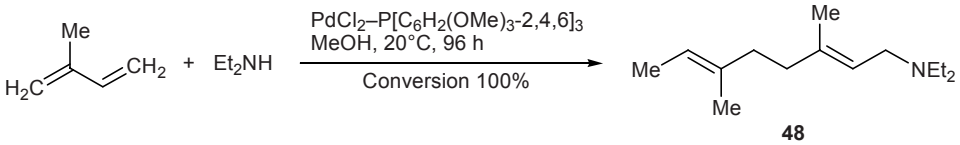
Hydroamination of isoprene with dialkylamines catalyzed by $Pd(acac)_2$–$P(OBu)_3$ (1 : 2) gave tail-to-

Scheme 14.



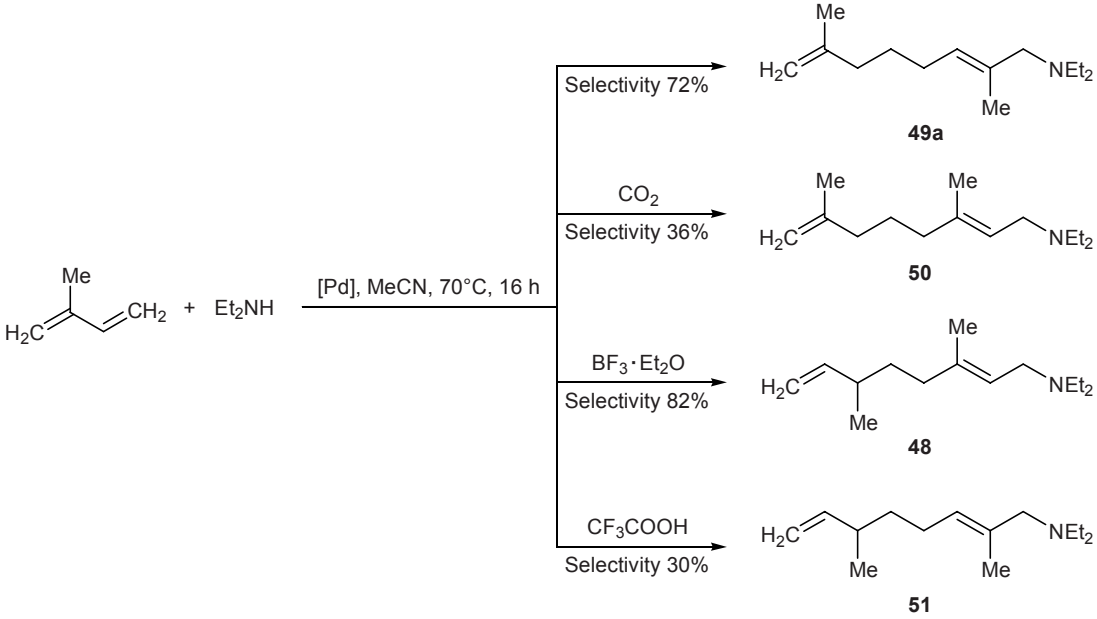
46 (95%) **47** (5%)

Scheme 15.



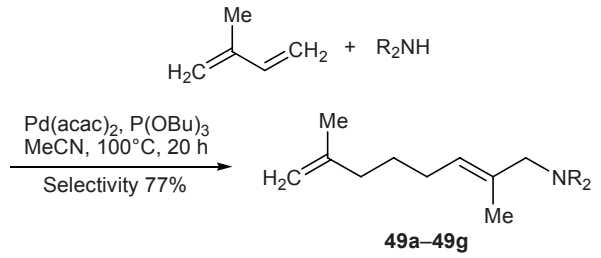
48

Scheme 16.



[Pd] = $Pd(acac)_2$–$P(C_6H_{11}$-*cyclo*$)_3$.

Scheme 17.



R = Et (**a**), Me (**b**), Pr (**c**), *i*-Pr (**d**), Bu (**e**), *i*-Bu (**f**); RR = $(CH_2)_5$ (**g**).

tail adducts **49a**–**49g** as the major products [42] (Scheme 17).

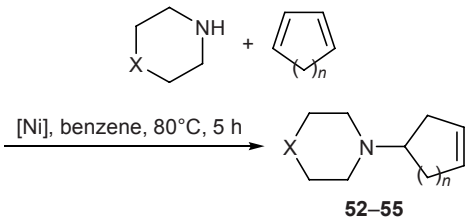
As concerns most practically important amino-substituted monoterpenes which contain natural isoprenoid fragment (**B**), selective procedures for their preparation were not reported so far. Compound **50** was previously synthesized with a selectivity of 31 [44], 36 [43], or 38% [45], and Maddok and Finn [46] recently succeeded in insignificantly increasing the selectivity (up to 41%).

The above data predetermine the necessity of developing highly active and selective metal complex catalysts for the synthesis of practically important regular alicyclic isoprenoid amines that are promising for the preparation of fragrant substances, preservatives, medicines, and agricultural agents.

4. HYDROAMINATION OF CYCLIC 1,3-DIENES

The synthesis of cycloalkenamines by reaction of cyclic 1,3-dienes (cyclopentadiene, cyclohexa-1,3-diene) with cyclic secondary amines in the presence of nickel-containing complexes was reported for the first time in [53–56]. Cyclopentadiene reacted with morpholine in the presence of $Ni(acac)_2$–$AlEt_3$–PBu_3–CF_3CO_2H (1 : 2 : 3 : 10, 80°C, 5 h) to give 60% of 1-(cyclopent-2-en-1-yl)morpholine (**52**). The yield of **52** is reduced due to side transformation of cyclopentadiene into dicyclopentadiene. Under analogous conditions, piperidine reacted with cyclopentadiene to produce 1-(cyclopent-2-en-1-yl)piperidine (**53**) in ~50% yield. The yields of amines **54** and **55** in the reactions of morpholine and piperidine with cyclohexa-1,3-diene were 80 and 90%, respectively (Scheme 18). Unlike cyclopentadiene, cyclohexa-1,3-diene reacted with piperidine and morpholine in the absence of trifluoroacetic acid as well, but the yields of the hydroamination products did not exceed 10%.

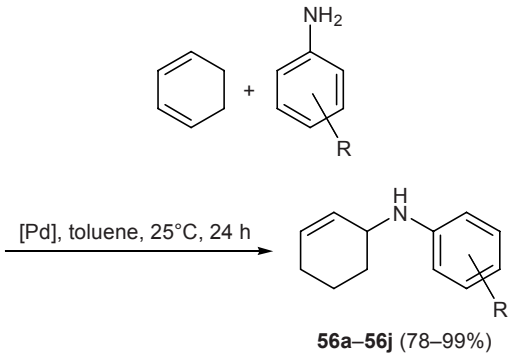
Scheme 18.



52, *n* = 1, X = O (yield 60%); **53**, *n* = 1, X = CH_2 (50%); **54**, *n* = 2, X = O (90%); **55**, *n* = 2, X = CH_2 (80%); [Ni] = $Ni(acac)_2$–PBu_3–$AlEt_3$–CF_3COOH.

Palladium complexes activated by trifluoroacetic acid were found to effectively catalyze hydroamination of cyclic 1,3-dienes with aniline and its derivatives [40, 57] (Scheme 19).

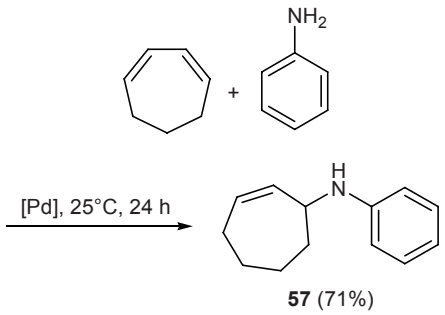
Scheme 19.



R = H (**a**), 2-Me (**b**), 3-Me (**c**), 4-Me (**d**), 4-CF_3 (**e**), 4-EtOCO (**f**), 2-MeO (**g**), 3-MeO (**h**), 4--MeO (**i**), 2-Br (**j**); [Pd] = $Pd(PPh_3)_4$–CF_3COOH, 1 : 5.

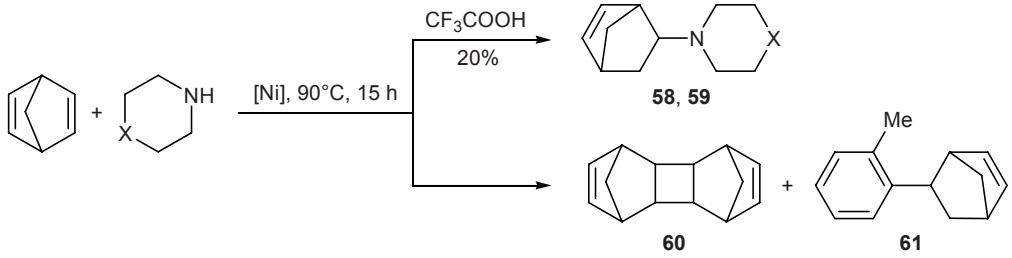
Hydroamination of cyclohepta-1,3-diene with aniline in the presence of $Pd(PPh_3)_4$ and a large excess of CF_3COOH gave *N*-(cyclohept-2-en-1-yl)aniline (**57**) in 71% yield [53] (Scheme 20). Cycloocta-1,3-diene failed to react under analogous conditions [53, 54]. Norbornadiene may be regarded as pseudoconjugated

Scheme 20.



[Pd] = $Pd(PPh_3)_4$–CF_3COOH, 1 : 5.

Scheme 21.



[Ni] = Ni(1,5-COD)$_2$–PBu$_3$; **58**, X = O; **59**, X = CH$_2$.

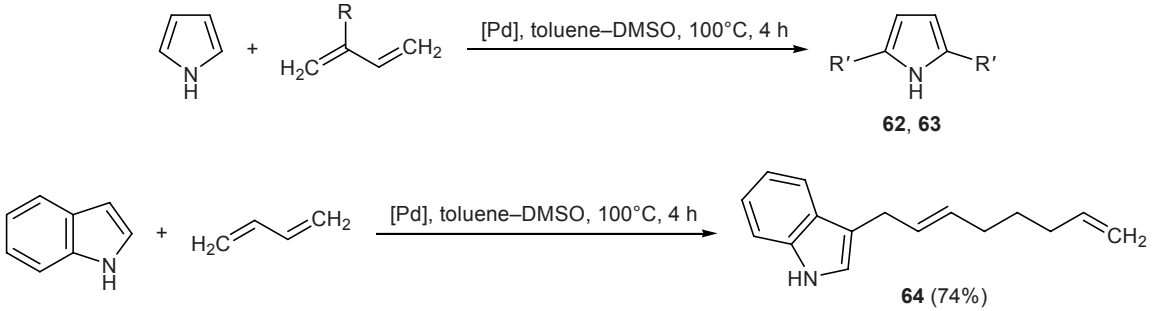
cyclic 1,4-diene; it smoothly reacted with morpholine and piperidine in the presence of Ni[(COD)]$_2$–PBu$_3$–CF$_3$COOH to form ~20% of the corresponding unsaturated amines **58** and **59** [58] (Scheme 21). In the absence of trifluoroacetic acid, the main reaction pathway was homodimerization of norbornadiene to [2+2]-cycloadduct **60** and *o*-tolylnorbornene **61** [58].

5. HYDROAMINATION OF 1,3-DIENES WITH AZA HETEROCYCLES CONTAINING AN N–H BOND

Five-membered nitrogen-containing heterocycles constitute another class of compounds having an N–H bond and potentially capable of reacting with 1,3-dienes to give hydroamination products. Catalytic hydroamination of 1,3-dienes with pyrrole, indole, imidazole, pyrazole, triazole, thiazole, thiadiazole, and their derivatives was studied in [59–70]. Pyrrole and indole reacted with butadiene at the activated C–H bond with formation of 2(5)-substituted pyrroles **62** and **63** and 3-substituted indole **64** (Scheme 22), while the N–H bond was not involved in the process [59].

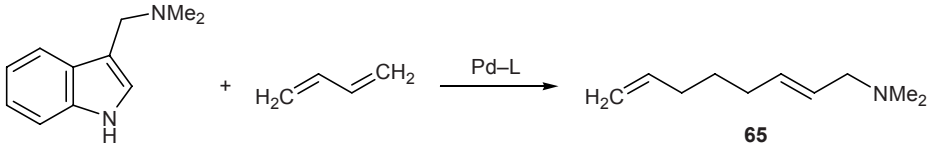
3-Substituted indoles such as 3-methyl-1*H*-indole (skatole) and methyl (1*H*-indol-3-yl)acetate did not react with butadiene and were completely recovered from the reaction mixtures. An exception was the reaction with *N*,*N*-dimethyl-1*H*-indol-3-ylmethanamine (gramine) which decomposed to give dimethylamine and tarry products; this pattern is quite typical of Mannich bases. Dimethylamine thus formed was quantitatively converted into *N*,*N*-dimethylocta-2,7-dien-1-amine (**65**) (Scheme 23). The inactivity of the NH group in the pyrrole molecule, as well as in molecules of its closest analogs having similar chemical properties (indole and its derivatives), was rationalized in

Scheme 22.

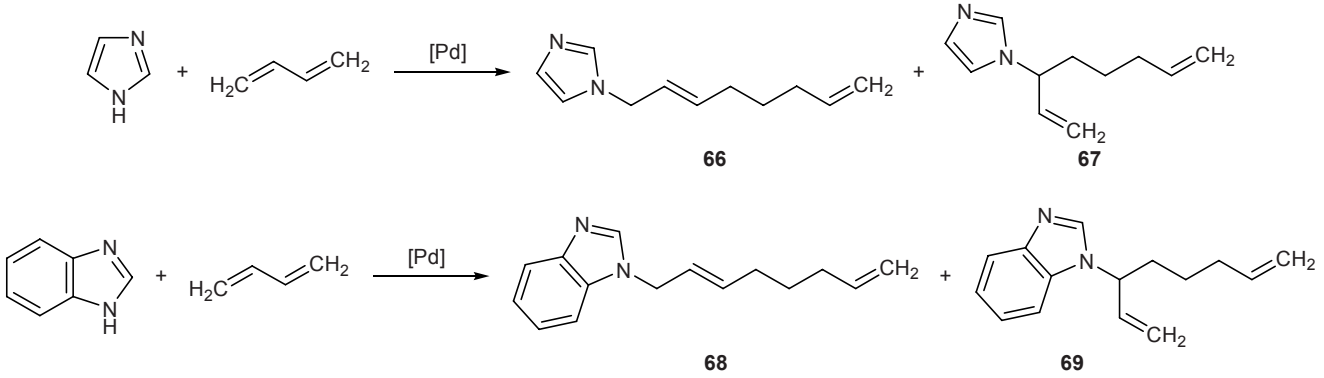


[Pd] = Pd(acac)$_2$–PPh$_3$–AlEt$_3$; R = H, Me; **62**, R′ = H$_2$C (90%); **63**, R′ = Me, H$_2$C, Me (30%).

Scheme 23.

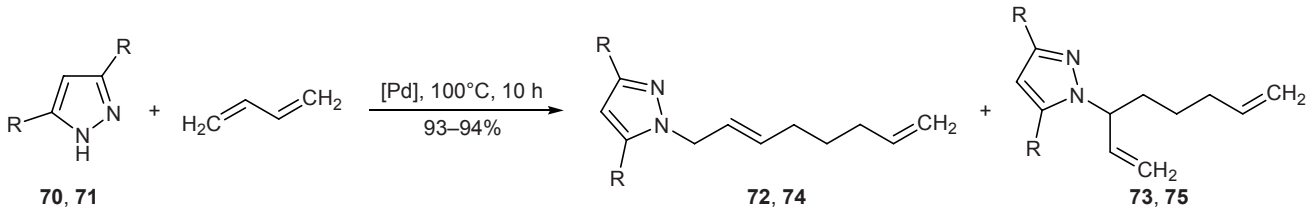


Scheme 24.



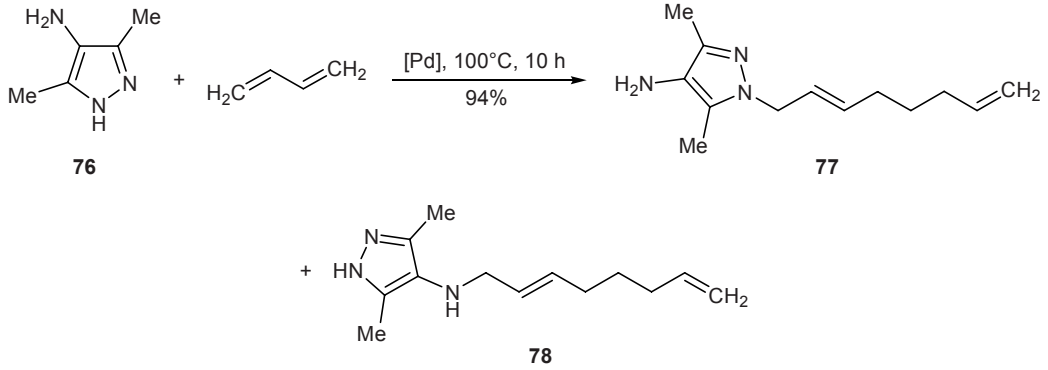
[Pd] = $Pd(acac)_2$–PPh_3–$AlEt_3$–CF_3COOH; 180°C, 10 h.

Scheme 25.



70, **72**, **73**, R = H; **71**, **74**, **75**, R = Me; [Pd] = $Pd(acac)_2$–PPh_3–$AlEt_3$–CF_3COOH.

Scheme 26.



[Pd] = $Pd(acac)_2$–PPh_3–$AlEt_3$–CF_3COOH; [**76**] : [$Pd(acac)_2$] = 10 : 1.

terms of low basicity of these compounds (pK_a 0.27). Imidazole and benzimidazole are stronger bases (pK_a 7.03 and 5.53, respectively), and they reacted with butadiene in the presence of palladium catalyst exclusively at the N–H bond to give an approximately equimolar mixture of isomeric octadienyl derivatives with overall yields of 92 (**66**, **67**) and 86% (**68**, **69**), respectively [60–63] (Scheme 24). Addition of trifluoroacetic acid to the catalytic system increased the catalytic activity of palladium complexes and reaction selectivity so that branched isomers **67** and **69** were formed with a selectivity of ~96%, the overall yield being 93–94% [60, 62]. Pyrazole and 3,5-dimethyl-1*H*-pyrazole turned out to be considerably less reactive in the hydroamination of butadiene, as compared to imidazole and benzimidazole. Pyrazole failed to react with butadiene in the presence of $Pd(acac)_2$–PPh_3–$AlEt_3$ (1 : 3 : 4). Addition of 5–10 mol of CF_3CO_2H per mole of $Pd(acac)_2$ made it possible to obtain the corresponding octa-2,7-dien-1-yl (**72**, **74**) and octa-1,7-dien-3-yl derivatives (**73**, **75**) in up to 94% yield (Scheme 25).

The reaction of 3,5-dimethyl-1*H*-pyrazol-4-amine (**76**) with butadiene in the presence of palladium

catalyst involved both the endocyclic N–H group and exocyclic amino group with formation of hydroamination products **77**and **78** [60] (Scheme 26).

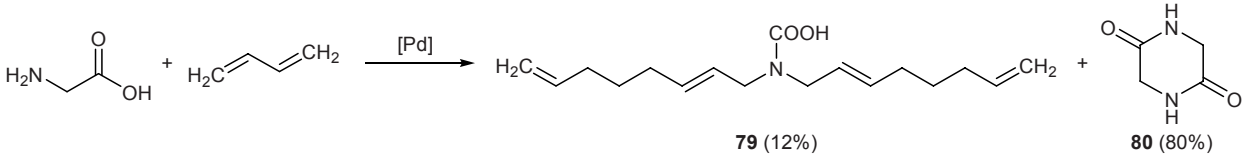
6. HYDROAMINATION OF BUTADIENE WITH AMINO ACIDS, AMINO ALCOHOLS, AND HYDROXYLAMINE

Hydroamination of 1,3-dienes with α-, β-, γ-, and ω-amino acids [61, 62, 71], amino alcohols [72–74], and hydroxylamine and its derivatives [62, 75, 76] leads to polyfunctionalized compounds possessing carboxy, hydroxy, and amino groups and unsaturated fragments. In addition, the effect of acid functionality (COOH, OH) on the reactivity of the N–H bond may be estimated. Among the above listed compounds, hydroamination of dienes with amino acids was studied most thoroughly. The simplest α-amino acid, glycine, reacted with butadiene at a ratio of 1 : 1 in DMSO in the presence of $Pd(acac)_2$–PPh_3–$AlEt_3$ to give ~12% of *N*,*N*-bis(octa-2,7-dien-1-yl)aminoacetic acid (**79**) [71]. Here, a considerable amount of initial glycine underwent dimerization to piperazine-2,5-dione (**80**) (Scheme 27). Under analogous conditions, α-alanine and butadiene (1 : 6) gave rise to a mixture of *N*-mono- and *N*,*N*-bis(octa-2,7-dien-1-yl)alanines **81** and **82** at a ratio of 32 : 68 (overall yield ~73%). Unlike glycine and α-alanine, α-aminobutyric acid reacted with butadiene to produce *N*-(octa-2,7-dien-1-y) derivative **83** in ~64% yield (Scheme 28). In the reactions of butadiene with proline and iminodiacetic acid, the corresponding *N*-(octa-2,7-dien-1-yl) derivatives **86**–**88** were obtained (Schemes 29, 30). These results indicate that extension of the hydrocarbon chain in α-amino acids increases the selectivity of hydroamination.

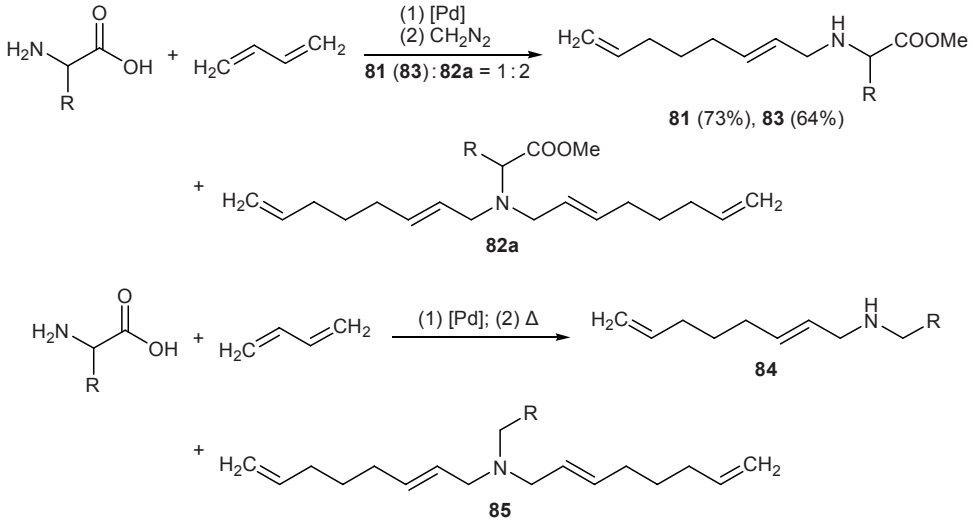
Vacuum distillation of the reaction mixtures obtained from butadiene and α-amino acids without preliminary separation of the catalyst was accompanied by decarboxylation of *N*-(octa-2,7-dien-1-yl) amino acids with formation of unsaturated amines **84** and **86** in high yield. Therefore, it is advisable to isolate butadiene telomers with amino acids as their methyl esters by treatment of the reaction mixture with diazomethane and subsequent fractional distillation under reduced pressure [61, 62, 71].

Another way of avoiding difficulties in the isolation of hydroamination products is to perform the reaction with preliminarily prepared amino acid esters. Butadiene reacted with glycine, alanine, and β-alanine ethyl esters in the presence of $Pd(acac)_2$–PBu_3–$AlEt_3$ (1 : 3 : 2), selectively yielding *N*,*N*-bis-octadienyl deriv-

Scheme 27.

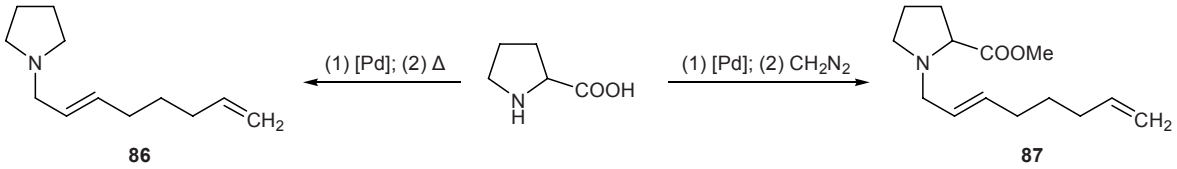


Scheme 28.

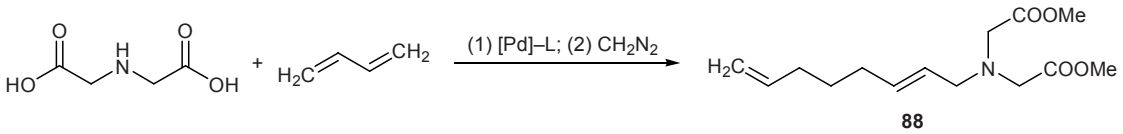


[Pd] = $Pd(acac)_2$–PPh_3–$AlEt_3$; toluene–DMSO (1 : 1.5), 100°C, 10 h; **81**, **82a**, **84**, **85**, R = Me; **83**, R = Et.

Scheme 29.

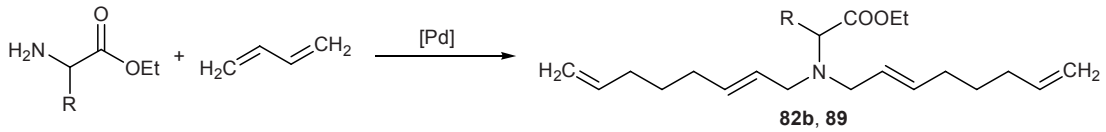


Scheme 30.

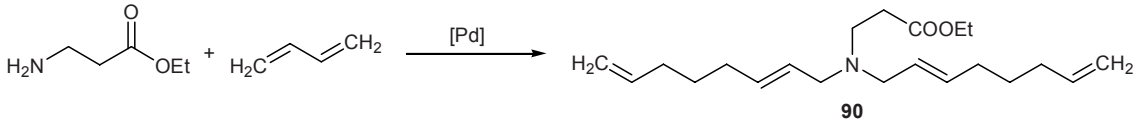


[Pd] = $Pd(acac)_2$–PPh_3–$AlEt_3$; toluene–DMSO (1 : 1.5), 100°C, 10 h.

Scheme 31.

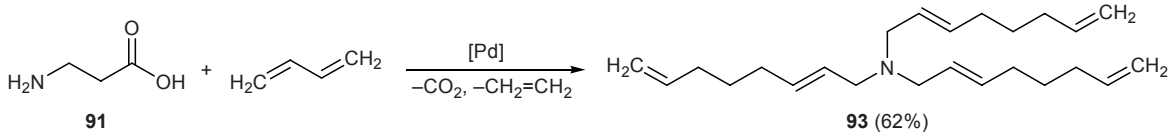


Scheme 32.

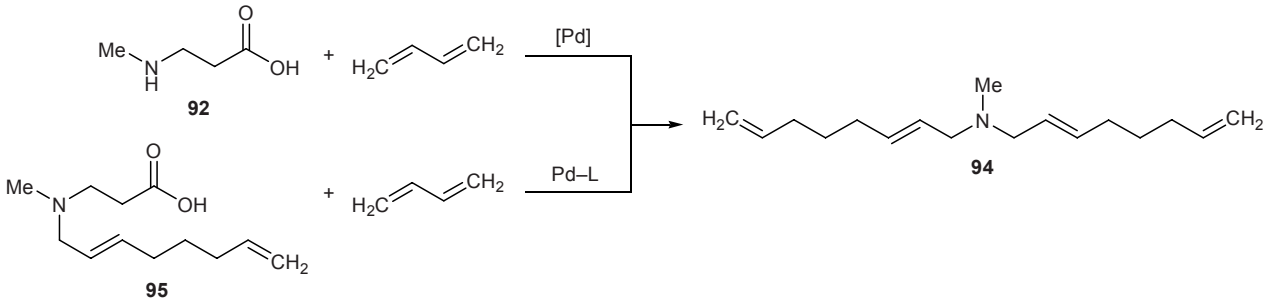


[Pd] = $Pd(acac)_2$–PBu_3–$AlEt_3$, 1 : 3 : 2; 100°C, 10 h; **82b**, R = Me; **89**, R = H.

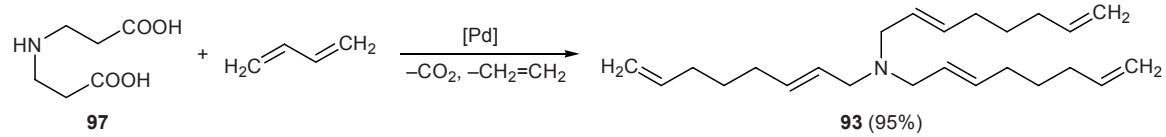
Scheme 33.



Scheme 34.

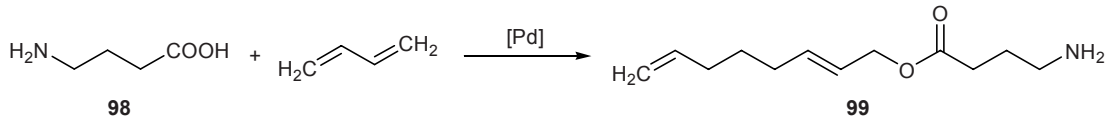


Scheme 35.



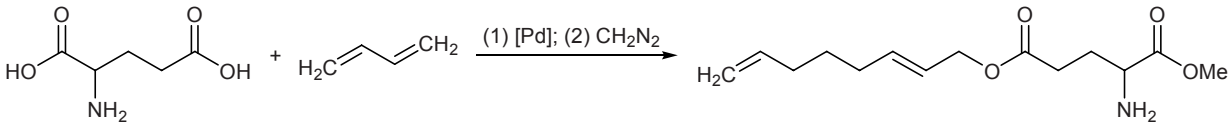
[Pd] = $Pd(acac)_2$–PPh_3–$AlEt_3$; 100°C, 10 h.

Scheme 36.



98 **99**

Scheme 37.



100 **101**

[Pd] = $Pd(acac)_2$–PPh_3–$AlEt_3$; 100°C, 10 h.

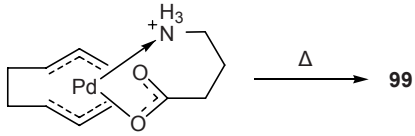
atives **82**, **89**, and **90** (90, 87, and 40%, respectively) [71] (Schemes 31, 32).

Hydroamination of butadiene with β-amino acids follows quite unusual pattern [71]. The reactions of β-alanine (**91**) and *N*-methyl-β-alanine (**92**) with butadiene gave in one step 62% of tris(octa-2,7-dien-1-yl)-amine (**93**) and 57% of *N*,*N*-bis(octa-2,7-dien-1-yl)-methanamine (**94**), respectively (Schemes 33, 34). Systematic study on the reactions of β-amino acids with butadiene showed that a necessary condition for cleavage of β-amino acids with liberation of carbon dioxide and ethylene is the presence of two methylene units on the nitrogen atom and of a free carboxy group.

Unlike *N*-methyl-β-alanine (**92**), *N*,*N*-dimethyl-β-alanine remained unchanged in the reaction with butadiene. Introduction of the second carboxy group into β-amino acid molecule favors more facile decarboxylation and elimination of ethylene. β,β′-Iminodipropionic acid (**97**) was thus converted into tris(octa-2,7-dien-1-yl)amine (**93**) in ~95% yield (Scheme 35). Presumably, alkylation of initial amino acid in the presence of palladium is followed by cleavage of the C–N and C–C bonds with elimination of ethylene, carbon dioxide, and octa-2,7-dien-1-amine. The latter reacts with butadiene, yielding tertiary amine **93** [71].

In contrast to α- and β-amino acids and their derivatives, γ-amino acids reacted with butadiene in the presence of palladium complexes at the carboxy group, while the amino group therein remained intact. For example, the reaction of γ-aminobutyric acid (**98**) with butadiene produced ~84% of unsaturated ester **99** (Scheme 36). Glutamic acid (**100**), being α- and γ-amino acid simultaneously, was converted to ester **101** (~67%; Scheme 37). The different path of reactions of γ-amino acids with butadiene is likely to be favored by formation of a six-membered transition state typical of cyclization of γ-amino acids to lactams, where the amino and carboxy groups of initial acid are involved in coordination to the central metal atom in the catalyst (complex **C4**). The subsequent attack on π-allylic electrophile by oxygen-centered nucleophile in complex **C4** leads to ester **99** (Scheme 38).

Scheme 38.



C4

α,ω-Amino acids having five and more methylene units between the COOH and NH_2 groups react with butadiene at the amino group [71]. 6-Aminohexanoic acid (**102**) reacted with butadiene to give *N*,*N*-bis(octa-2,7-dien-1-yl)-6-aminohexanoic acid which was identified as methyl ester **103** (Scheme 39). Apart from ester **103**, 1-(octa-2,7-dien-1-yl)azepan-2-one (**104**) was isolated from the reaction mixture. Presumably, compound **104** was formed via intramolecular condensation of *N*-(octa-2,7-dien-1-yl)-6-aminohexanoic acid in the presence of palladium complexes or as a result of thermal reaction. Caprolactam failed to react with butadiene under analogous conditions [71].

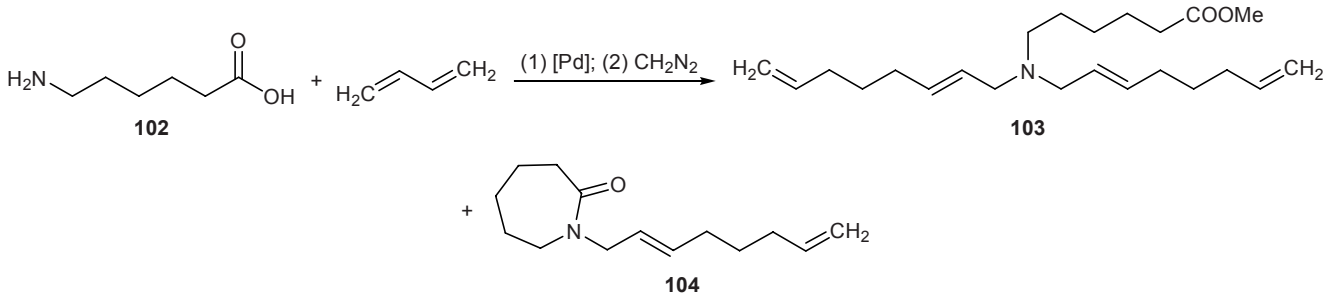
Fakhretdinov et al. [62, 71] compared the reactivities of aliphatic and aromatic amino acids in the hydroamination of butadiene catalyzed by palladium complexes. *o*-, *m*-, and *p*-Aminobenzoic acids behaved generally similarly to aliphatic α-amino acids. Depending on the conditions, both unsaturated aromatic amine **13** and *N*-(octa-2,7-dien-1-yl) derivatives **105**–**107** were obtained (Scheme 40).

The use of *N*-methylpyrrolidin-2-one as solvent ensured successful hydroamination of butadiene with

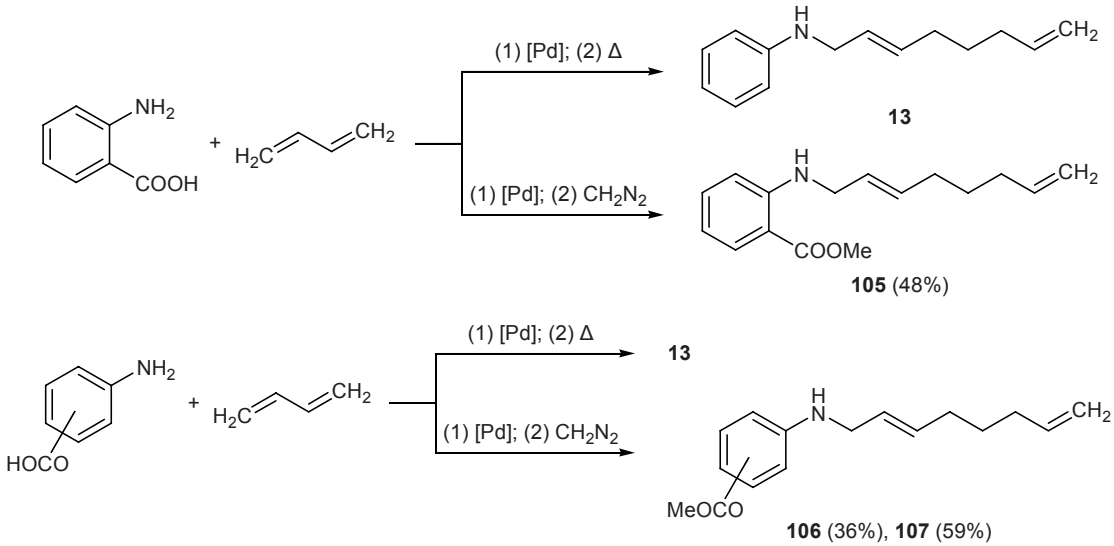
hydroxylamine [75]. The reaction was carried out in the presence of $Pd(acac)_2$–PPh_3–$AlEt_3$–CF_3CO_2H (1:3:4:5; 90°C, 8 h) using 6 equiv of butadiene, and the products were *N*,*N*-bis(octa-2,7-dien-1-yl)hydroxylamine (**108**), tris(octa-2,7-dien-1-yl)amine (**93**) and octa-2,7-dien-1-ol (**109**) (overall yield ~51%); the fraction of compound **108** in the product mixture reached ~59% (Scheme 41). Tris(octa-2,7-dien-1-yl)amine (**93**) and octa-2,7-dien-1-ol (**109**) are products of butadiene telomerization with ammonia and water, respectively; they were likely to be formed as a result of decomposition of hydroxylamine into ammonia and water.

The effect of substituent on the nitrogen atom was studied in telomerization of butadiene with *N*-alkyl- and *N*-arylhydroxylamines. Phenylhydroxylamine reacted with butadiene to give ~68% of *N*-(octa-2,7-dien-1-yl)-*N*-phenylhydroxylamine (**110**) and 16% of *N*-(but-2-en-1-yl)-*N*-phenylhydroxylamine (**111**) [62, 75]. *N*,*N*-Bis(octa-2,7-dien-1-yl)methanamine (**112**) was obtained with high selectivity from methyl-

Scheme 39.

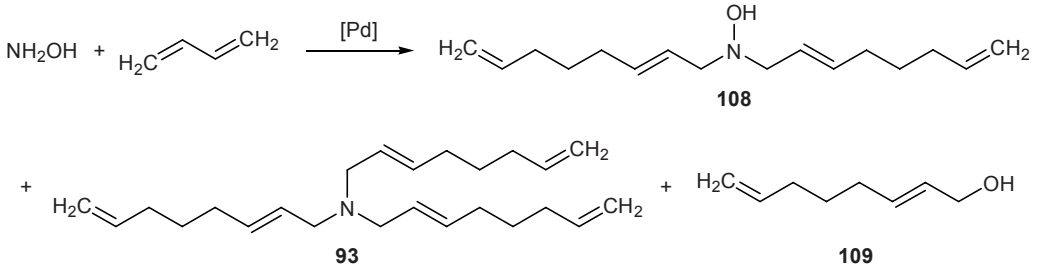


Scheme 40.

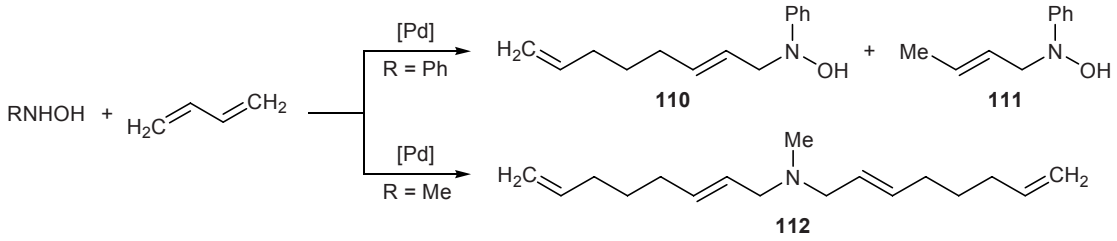


[Pd] = $Pd(acac)_2$–PPh_3–$AlEt_3$; 100°C, 10 h; **106**, *m*-COOMe; **107**, *p*-COOMe.

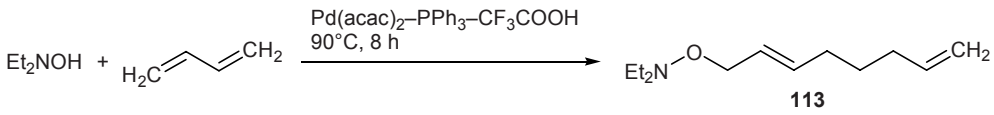
Scheme 41.



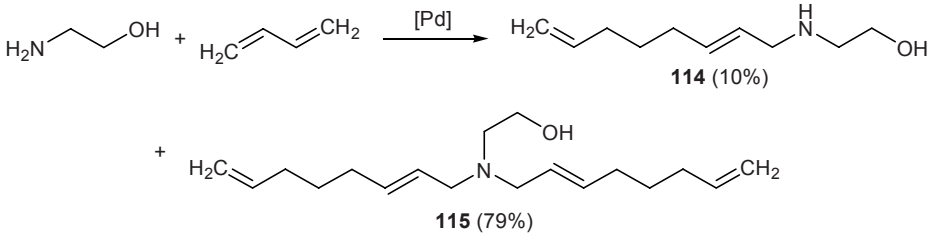
Scheme 42.



Scheme 43.

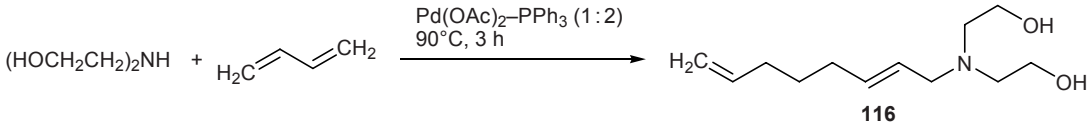


Scheme 44.

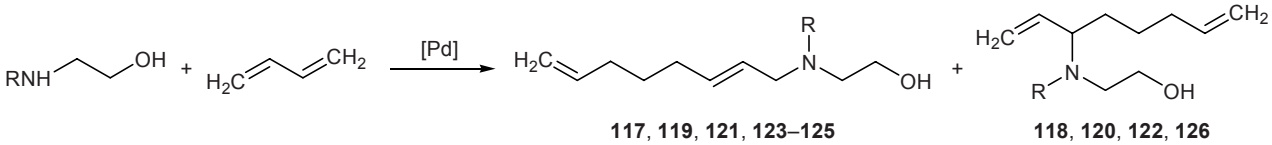


[Pd] = $Pd(PPh_3)_2$–maleic anhydride; 100°C, 3 h, *t*-BuOH, amino alcohol–diene ratio 1:2.

Scheme 45.

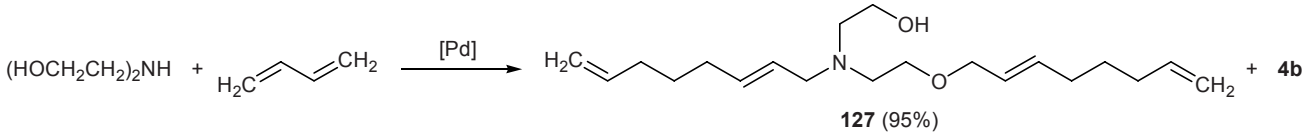


Scheme 46.



[Pd] = $Pd(OAc)_2$–PPh_3; 80°C, 16 h; **117**, R = Me (98%); **118**, R = Me (2%), **119**, R = Et (98.5%); **120**, R = Et (1.5%); **121**, R = Bu (98%); **122**, R = Bu (2%); **123**, R = *t*-Bu (99%); **124**, R = Ph (93%), **125**, R = $PhCH_2$ (97%); **126**, R = $PhCH_2$ (3%).

Scheme 47.



[Pd] = $Pd(OAc)_2$–PPh_3–Et_3N; 80°C, 16 h.

hydroxylamine; obviously, compound **112** was formed via reaction with methylamine arising from decomposition of methylhydroxylamine [75]. N,N-Disubstituted hydroxylamines were converted into the corresponding *O*-octadienyl ethers in satisfactory yield. Diethylhydroxylamine and butadiene gave rise to *N*,*N*-diethyl-*O*-(octa-2,7-dien-1-yl)hydroxylamine (**113**) in ~28% yield [62, 75] (Scheme 43).

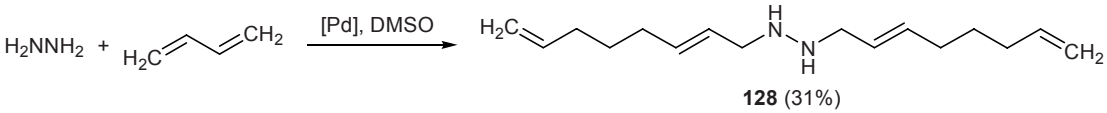
Hydroamination of butadiene with amino alcohols and their derivatives is promising from the viewpoint of synthesis of individual N- and O-substituted unsaturated polyfunctional heteroatom compounds and secondary and tertiary amines whose preparation by other methods is difficult and laborious.

Amino alcohols possess two different functional groups with a labile hydrogen atom. Depending on their structure, they can react with butadiene at both N–H and O–H bonds yielding compounds **114**–**127** [72–74] (Schemes 44–47). Umpleby [72] succeeded in involving both NH and OH groups in amino alcohols simultaneously in the hydroamination of butadiene using a large excess of the latter (9 equiv). Excess butadiene was converted into its linear dimer, octa-1,3,7-triene (**4b**) (Scheme 47).

7. HYDROAMINATION OF 1,3-DIENES WITH HYDRAZINE AND ITS DERIVATIVES

First attempts to effect hydroamination of 1,3-dienes with hydrazine and its derivatives in the presence of $Pd(acac)_2$–PPh_3–$AlEt_3$–CF_3COOH were unsuccessful. Under typical conditions (100°C, 8 h, benzene), hydrazine hydrate decomposed into nitrogen and hydrogen. Simultaneously, Pd^{2+} was reduced to metallic

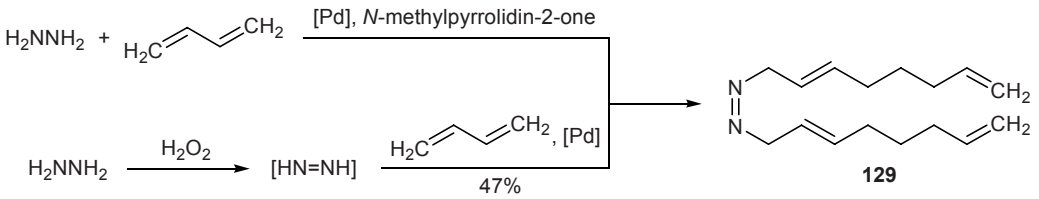
Scheme 48.



128 (31%)

[Pd] = $Pd(acac)_2$–$(Ph_2PCH_2)_2$–$AlEt_3$–CF_3COOH; 90°C, 8 h.

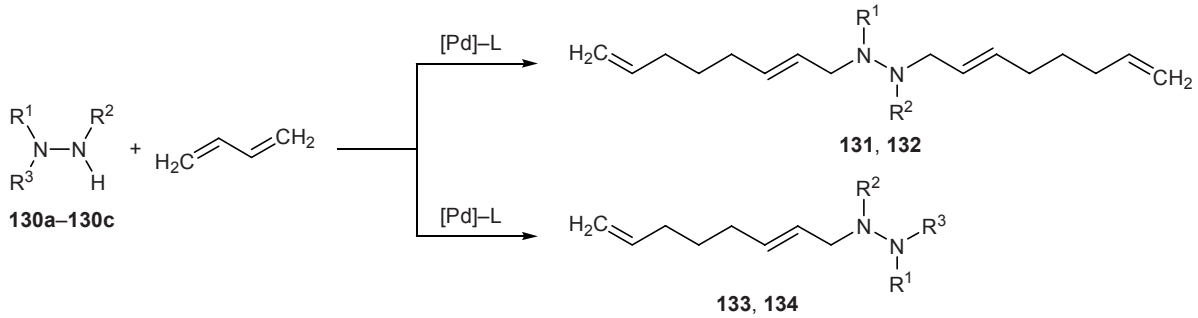
Scheme 49.



129

[Pd] = $Pd(acac)_2$–PBu_3–$AlEt_3$–CF_3COOH, 1 : 3 : 4 : 5; 90°C, 8 h.

Scheme 50.



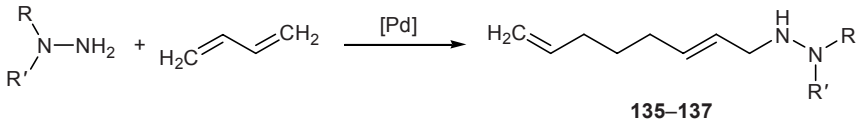
130a–130c

131, **132**

133, **134**

130a, R^1 = Et, R^2 = R^3 = H; **131**, R^1 = Et, R^2 = H; **132**, R^1 = R^2 = Me; **130b**, **134**; R^1 = R^2 = Me, R^3 = H; **130c**, **133**, R^1 = R^3 = Me, R^2 = H.

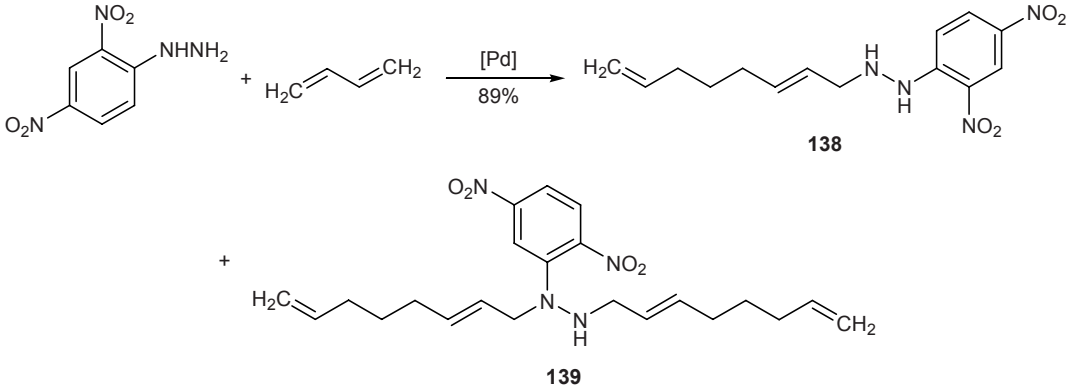
Scheme 51.



135–137

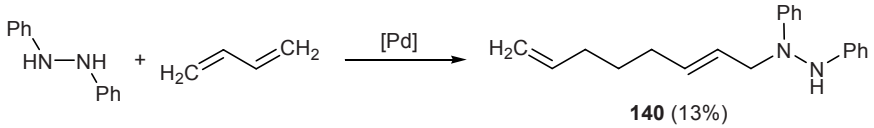
135, R = H, R′ = Ph (96%); **136**, R = Me, R′ = Ph (96%); **137**, R = H, R′ = naphthyl (80%).

Scheme 52.



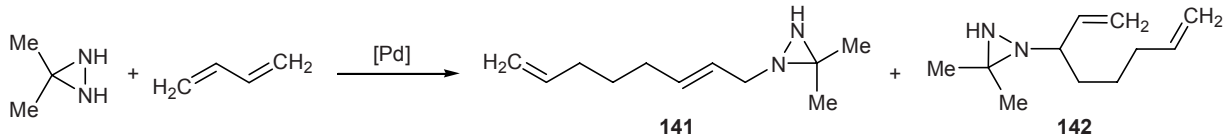
Ratio **138**:**139** = 1:3.

Scheme 53.



[Pd] = $Pd(acac)_2$–PPh_3–$AlEt_3$–CF_3COOH; DMSO, DMF, HMPA, 100°C, 8 h.

Scheme 54.



[Pd] = $Pd(acac)_2$–PPh_3–$AlEt_3$–CF_3COOH; toluene, 60°C, 6 h.

palladium which separated as a disperse powder. The problem of involving hydrazine in hydroamination of butadiene was solved [77, 78] by proper choice of solvent (dimethyl sulfoxide, dimethylformamide, *N*-methylpyrrolidin-2-one, HMPA, tetramethylurea) capable of stabilizing catalytically active low-valence Pd^0 and Pd^+ species via coordination. The major product in the reaction of butadiene with hydrazine in DMSO was *N*,*N*′-bis(octa-2,7-dien-1-yl)hydrazine (**128**) whose yield reached ~31% [77] (Scheme 48).

Butadiene reacted with hydrazine hydrate in such solvents as HMPA, tetramethylurea and *N*-methylpyrrolidin-2-one in quite unusual fashion. The product had the structure of (6*E*,9*Z*,12*E*)-9,10-diazaoctadeca-1,6,9,12,17-pentaene (**129**, yield 52–65%; Scheme 49). It was presumed that the initial reaction step is dehydrogenation of hydrazine over palladium catalyst and that diazene thus formed reacts with butadiene to form compound **129**. The reaction of butadiene with diazene preliminarily generated *in situ* by oxidation of hydrazine with hydrogen peroxide in the presence of Cu salt gave 47% of diaazapolyene **129** [61, 62, 77].

Unlike hydrazine hydrate, substituted hydrazines **130a**–**130c** reacted with butadiene under the above conditions to produce exclusively *N*-(octa-2,7-dien-1-yl)hydrazines, whereas no azo compounds were detected among the products [77] (Scheme 50). Ethylhydrazine (**130a**) and butadiene gave rise to *N*-ethyl-*N*,*N*′-bis(octa-2,7-dien-1-yl)hydrazine (**131**) in ~22% yield. From symmetric *N*,*N*′-dimethylhydrazine (**130b**) and butadiene, a mixture of *N*-mono- and *N*,*N*′-bis(octa-2,7-dien-1-yl)hydrazines **132** and **134** was obtained in an overall yield of ~94%. Unsymmetrical *N*,*N*-dimethylhydrazine (**130c**) was converted with high selectivity into *N*,*N*-dimethyl-*N*′-(octa-2,7-dien-1-yl)hydrazine (**133**; yield ~88%).

Arylhydrazines were more reactive than unsubstituted hydrazine and alkylhydrazines in the hydroamination of butadiene, and they reacted with butadiene even in the absence of trifluoroacetic acid to

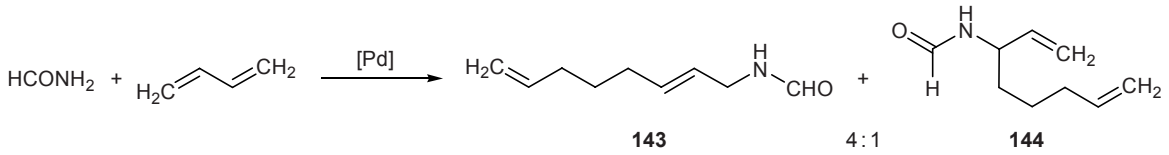
afford the corresponding *N*-(octa-2,7-dien-1-yl) derivatives. Likewise, compounds **135**–**137** were formed in 80–96% yield in the reactions of butadiene with *N*-methyl-*N*-phenylhydrazine, phenylhydrazine, and naphthalen-2-ylhydrazine in the presence of $Pd(acac)_2$–PPh_3–$AlEt_3$ [77] (Scheme 51). Introduction of nitro groups into the benzene ring of phenylhydrazine (2,4-dinitrophenylhydrazine) favored formation of *N*,*N*′-bis(octa-2,7-dien-1-yl) derivative **139** in the reaction with butadiene (Scheme 52). Symmetric 1,2-diphenylhydrazine was less reactive toward butadiene, presumably due to reduced basicity and steric hindrances created by bulky phenyl substituents: the reaction gave only ~13% of *N*-(octa-2,7-dien-1-yl)-*N*,*N*′-diphenylhydrazine (**140**) (Scheme 53).

3,3-Dimethyldiaziridine may be regarded as structural analog of 1,2-dialkylhydrazines; its reaction with butadiene involved difficulties, and the product was a mixture of compounds **141** and **142** (overall yield 40%). Here, only one NH group was involved in the process which was accompanied by decomposition of the initial compound into N_2, H_2, and propylene [79] (Scheme 54).

8. HYDROAMINATION OF 1,3-DIENES WITH CARBOXYLIC ACID AMIDES AND IMIDES

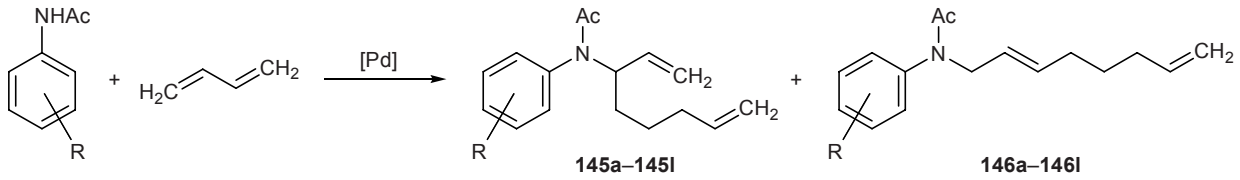
The results of studying catalytic hydroamination of 1,3-dienes with aliphatic and aromatic carboxylic acid amides and imides were reported in [80]. The reaction of formamide with butadiene in the presence of $Pd(acac)_2$–PPh_3–$AlEt_3$–CF_3COOH ($Pd:CF_3COOH$ = 1:5) gave a mixture of *N*-(octa-2,7-dien-1-yl)- and *N*-(octa-1,7-dien-3-yl)formamides **143** and **144** in an overall yield of ~17% (Scheme 55). Raising the temperature to 110°C increased the overall yield of amides **143** and **144** to 32%. Their yield also increased when the reaction was performed in a polar solvent (dimethylformamide or dimethyl sulfoxide). The yield reached 67% even in the absence of trifluoroacetic

Scheme 55.



[Pd] = $Pd(acac)_2$–PPh_3–$AlEt_3$–CF_3COOH; 80°C.

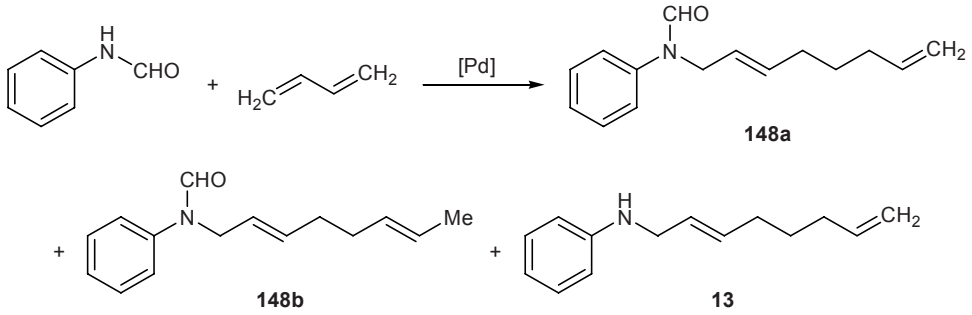
Scheme 56.



[Pd] = $Pd(acac)_2$–PPh_3–$AlEt_3$; 100°C, 7–9 h.

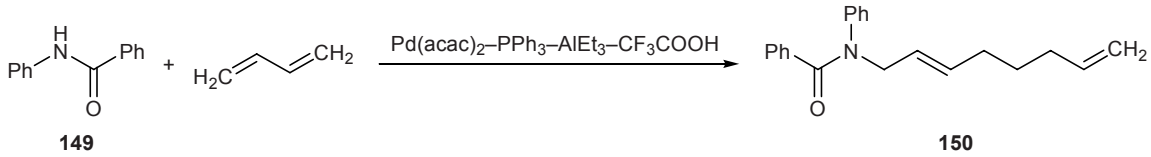
R	Overall yield, %	Product ratio
H	26	**145a**, **146a**, 1:24
2-Me	58	**145b**, **146**, 1:18
3-Me	10	**145c**, **146c**, 2:1
4-Me	18	**145d**, **146d**, 1:30
4-NH_2	74	**145e**, **146e**, 1:1.25
3-NH_2	74	**145f**, **146f**, 1:3.3
4-MeO	74	**145g**, **146g**, 7:10
3-O_2N	78	**145h**, **146h**, 1:35
4-O_2N	75	**145i**, **146i**, 2.4:1
2-O_2N	70	**145j**, **146j**, 1:32
2-Ph	50	**145k**, **146k**, 1:25
3-F	76	**145l**, **146l**, 1:75

Scheme 57.

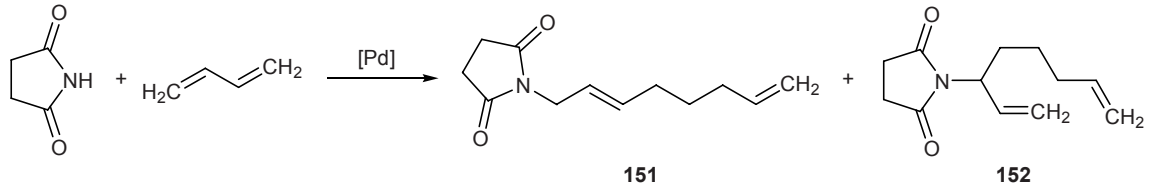


Ratio **148a**:**148b**:**13** = 2.5:1:9; overall yield 30%.

Scheme 58.



Scheme 59.

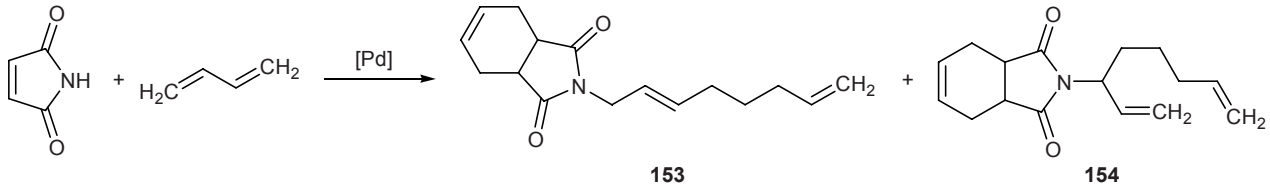


acid. However, in this case the reaction was accompanied by formation of 35% of tris(octa-2,7-dien-1-yl)amine (**93**), presumably as a result of decomposition of formamide with liberation of ammonia. In fact, special experiments showed that formamide decomposed on heating in the catalytic system $Pd(acac)_2$–PPh_3–$AlEt_3$ with quantitative formation of NH_3 and CO.

The reactions of butadiene with acetanilide and its derivatives substituted at the aromatic ring followed an analogous pattern. The conversion, yields of **145** and **146**, and selectivity strongly depended on the substituent nature [81] (Scheme 56). The reaction with formanilide (**147**) was accompanied by formation of *N*-(octa-2,7-dien-1-yl)aniline (**13**) (Scheme 57); obviously, this side reaction was preceded by decomposition of formanilide into carbon(II) oxide and aniline. The hydroamination of butadiene with benzanilide (**149**) was characterized by very high selectivity, and *N*-(octa-2,7-dien-1-yl)-*N*-phenylbenzamide (**150**) was obtained in ~80% yield [81] (Scheme 58). The use of a polar solvent, e.g., DMF, is a necessary condition for butadiene to react with aliphatic and cyclic imides [81]. For instance, succinimide reacted with butadiene at a ratio of 1:2 in the presence of $Pd(acac)_2$–PPh_3–$AlEt_3$ (1:3:4) in DMF at 110°C (9 h) to form 67% of a mixture of *N*-(octa-2,7-dien-1-yl)- and *N*-(octa-1,7-dien-3-yl)succinimides **151** and **152** at a ratio of 7:2 [81] (Scheme 59). Under analogous conditions, maleimide and butadiene (1:3) gave rise to *N*-octadienyltetrahydrophthalimides **153** and **154** in an overall yield of 71% (Scheme 60). Molecules **153** and **154** contain an additional cyclohexene ring arising from the Diels–Alder reaction of butadiene with maleimide. Compounds **153** and **154** were also obtained by hydroamination of butadiene with tetrahydrophthalimide (**155**) which was preliminarily prepared in almost quantitative yield by heating a mixture of butadiene and maleimide (1.5:1) (Scheme 61).

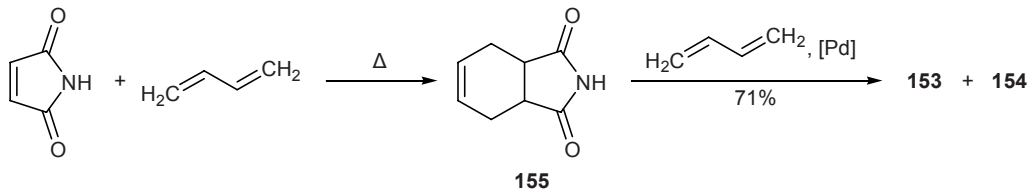
The reaction sequence changes in going from butadiene to isoprene and piperylene. Isoprene reacted with maleimide to give 4-methyltetrahydrophthalimide (**156**) and *N*-(2,7-dimethylocta-2,7-dien-1-yl)maleimide (**157**), i.e., the N–H bond in compound **156** was completely deactivated due to the presence of a methyl group in position *4*, which was quite surprising [81] (Scheme 62). Analogous reaction of maleimide with

Scheme 60.



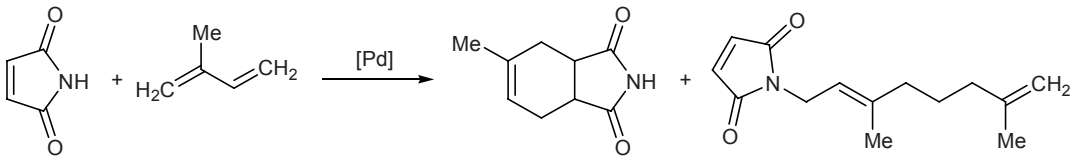
153 **154**

Scheme 61.



155

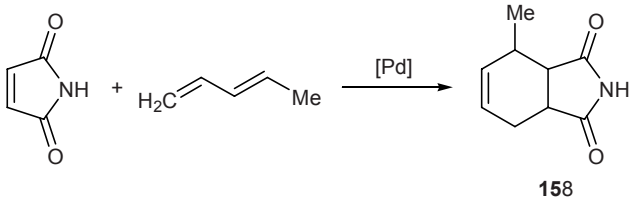
Scheme 62.



156 (66%) **157**

piperylene stopped at the stage of formation of Diels–Alder adduct **158** [81] (Scheme 63).

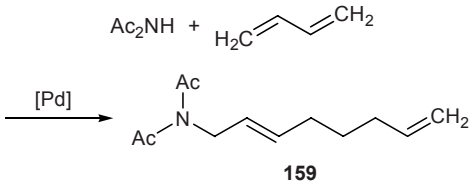
Scheme 63.



158

Hydroamination of butadiene with acyclic amides occurred fairly smoothly. The reaction of butadiene with diacetamide gave only one of possible isomers, *N*-(octa-2,7-dien-1-yl)diacetamide (**159**) with 100% selectivity [81] (Scheme 64).

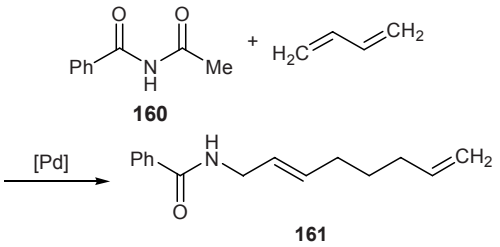
Scheme 64.



159

Butadiene reacted with *N*-acetylbenzamide (**160**) in tetramethylurea in unusual mode. The reaction was accompanied by elimination of the acetyl group, and it resulted in selective formation of *N*-(octa-2,7-dien-1-yl)benzamide (**161**) [81] (Scheme 65).

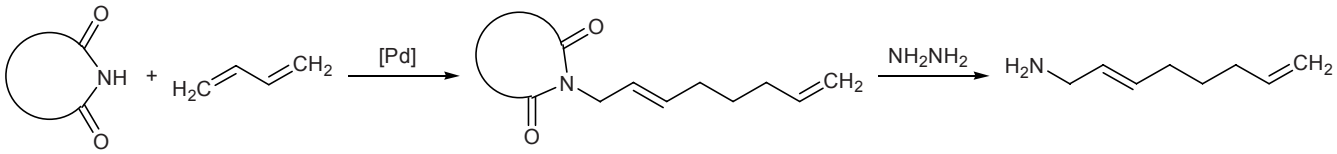
Scheme 65.



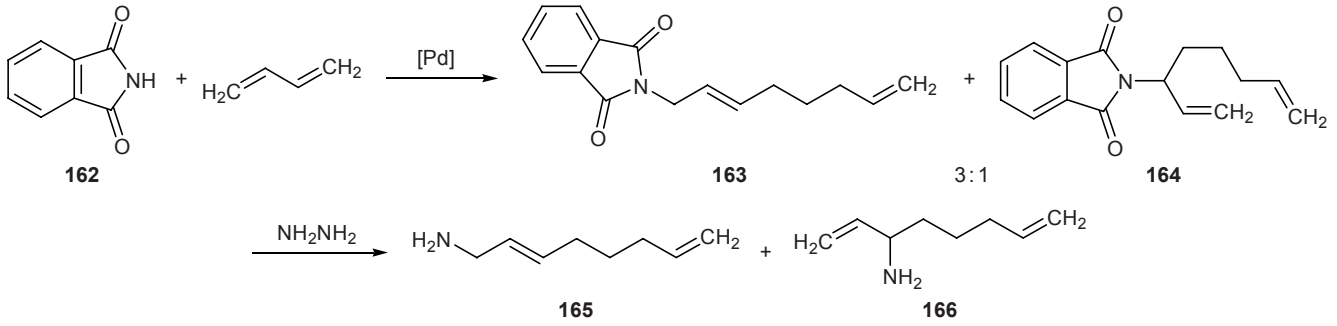
160 **161**

The presence in carboxylic acid imide molecules of only one N–H bond exhibiting high reactivity in the hydroamination of 1,3-dienes, makes it possible to use them for selective preparation of primary amines as shown in Scheme 66. An example of such synthesis with phthalimide (**162**) was described in [82]. The reaction of **162** with 4 equiv of butadiene gave a mixture of *N*-(octa-2,7-dien-1-yl)- and *N*-(octa-1,7-dien-3-yl)phthalimides **163** and **164** in an overall yield of 95%; the subsequent reduction with hydrazine hydrate afforded unsaturated primary amines **165** and **166** in 60% yield (Scheme 67). Analogous reaction of phthalimide with isoprene resulted in the formation of *N*-(2,7-dimethylocta-2,7-dien-1-yl)phthalimide (**167**, 55%) as the major product [41] (Scheme 68). Piperylene reacted with phthalimide much more difficultly,

Scheme 66.

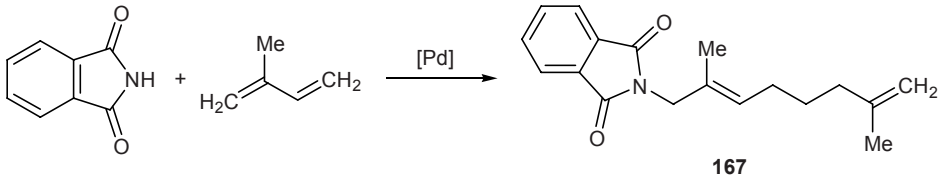


Scheme 67.

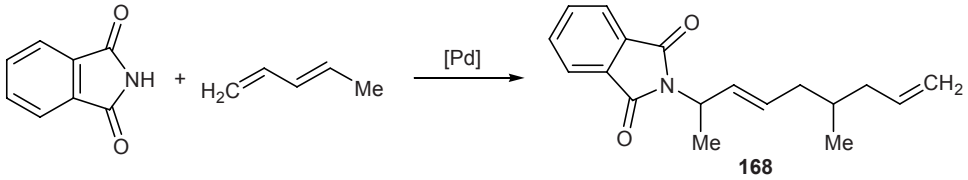


[Pd] = $Pd(acac)_2$–$P(OBu)_3$–$AlEt_3$, 1 : 3 : 4; tetramethylurea, 100°C, 9 h.

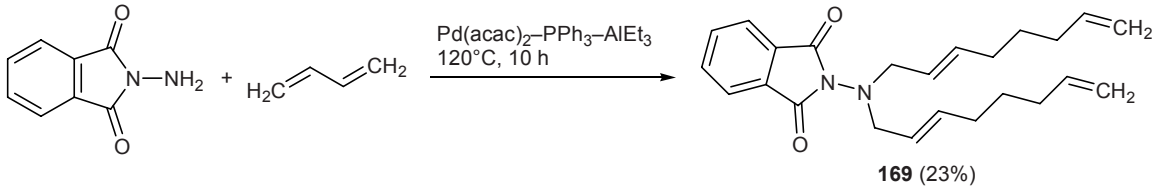
Scheme 68.



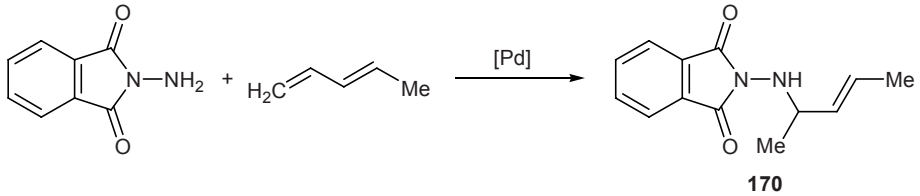
Scheme 69.



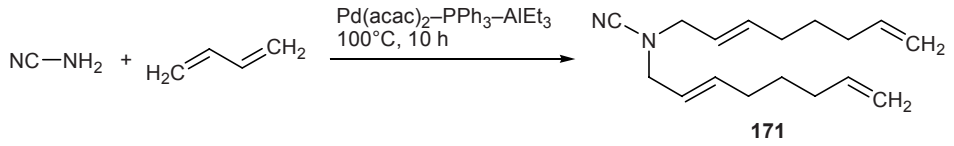
Scheme 70.



Scheme 71.



Scheme 72.



171

and unsaturated adduct **168** was obtained in a poor yield (11%) (Scheme 69).

N-Aminophthalimide possessing an N–N fragment behaves similarly to hydrazine; its reaction with butadiene occurs only in polar aprotic solvents (DMSO, DMF) with formation of 23% of compound **169** (Scheme 70). The corresponding 1 : 1 adduct, *N*-(1-methylbut-2-en-1-ylamino)phthalimide (**170**) was obtained in ~15% yield from *N*-aminophthalimide and (*E*)-piperylene under analogous conditions (Scheme 71). Hydroamination of butadiene with cyanamide attracted considerable interest from the practical viewpoint. The product of this reaction was *N*,*N*-bis(octa-2,7-dien-1-yl)cyanamide (**171**, yield ~45%) which was formed with high selectivity (Scheme 72).

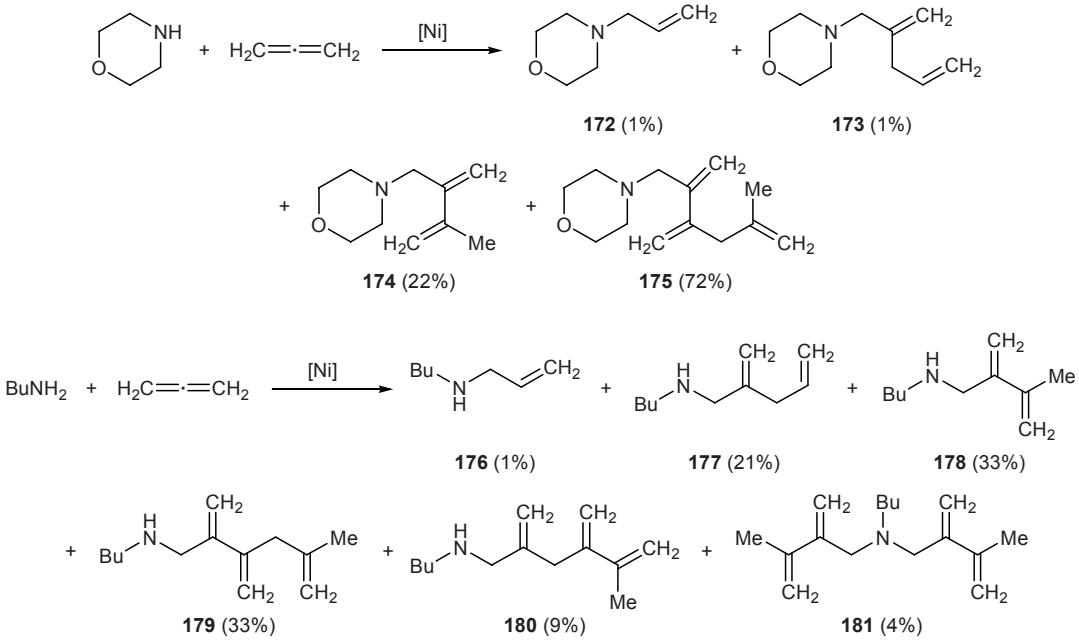
Thus hydroamination of 1,3-dienes with carboxylic acid amides and imides opens synthetic routes to unsaturated functionally substituted monomers that are promising as starting materials for the preparation of ion exchangers, light-sensitive polymeric materials, selective sorbents, as well as of difficultly accessible unsaturated primary amines.

9. HYDROAMINATION OF ALLENES

Allene and some its derivatives were found to be fairly reactive in the catalytic hydroamination [83–92]. Nickel, palladium, rhodium, zirconium, and lanthanide complexes were used to catalyze reactions of allenes with amines. Primary and secondary amines reacted with allene in the presence of nickel-containing catalytic systems with formation of complex mixtures of unsaturated amines **172**–**181** (Scheme 73). Among these products, the most interesting from the viewpoint of further transformations were isomers **174**, **178**, and **181** containing a 1,3-diene fragment. More complex composition of the hydroamination products obtained from allene and primary amines may be rationalized taking into account that the reaction involves both N–H bonds in the amine; an example is the formation of 4 : 1 adduct **181**.

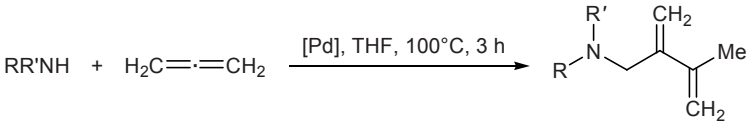
Palladium-containing catalysts ensured higher selectivity, as compared to nickel complexes, in the hydroamination of allene with both secondary and primary amines [83, 84]. These reactions gave com-

Scheme 73.



[Ni] = $NiBr_2$–$PPh(OPr\text{-}i)_2$; EtOH, 160°C, 1 h.

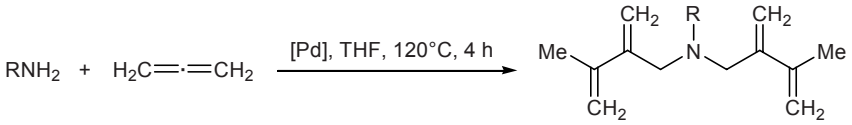
Scheme 74.



182a–182m

R = H, R′ = Me (**a**, 42%), Et (**b**, 29%), *i*-Pr (**c**, 44%), Pr (**d**, 30%), *t*-Bu (**e**, 32%), 1-Ad (**f**, 75%), *cyclo*-C_6H_{11} (**g**, 75%), Ph (**h**, 12%); R = R′ = Me (**i**, 70%), Et (**j**, 77%); RR′N = pyrrolidin-1-yl (**k**, 78%), piperidino (**l**, 79%), morpholino (**m**, 42%).

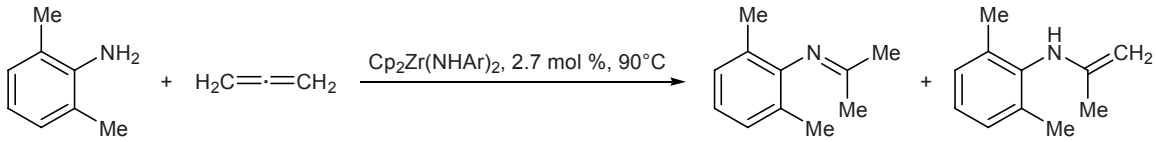
Scheme 75.



183 (55%), **184** (66%)

183, R = Me; **184**, R = Et; [Pd] = $Pd(PPh_3)_2$–maleic anhydride.

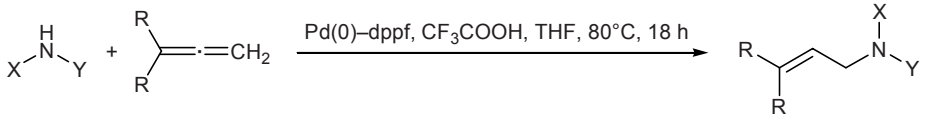
Scheme 76.



185a (83%) **185b**

Ar = 2,6-$Me_2C_6H_3$.

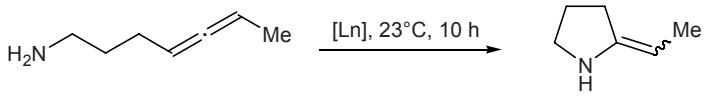
Scheme 77.



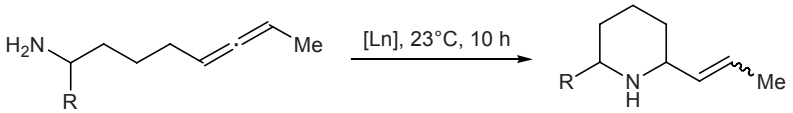
186a–186h

X = Y = $EtOCOCH_2$, R = Ph (**a**, 60%), 4-MeC_6H_4 (**b**, 73%), 4-$F_3CC_6H_4$ (**c**, 67%); RR = CH_2CH_2 (**d**, 83%); X = Y = $PhCH_2$, R = 4-MeC_6H_4 (**e**, 99%), 4-$F_3CC_6H_4$ (**f**, 75%); R = 4-MeC_6H_4, X = Y = Ph (**g**, 67%); R = Ph, X = Ph, Y = naphthyl (**h**, 62%).

Scheme 78.



187 (95%, *Z*:*E* = 86:14)

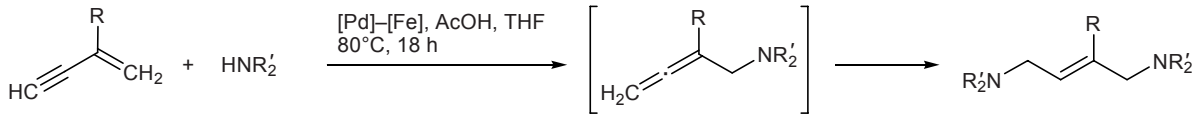


188a (95%, *Z*:*E* = 80:20)
188b (95%, *Z*:*E* = 55:45)

[Ln] = $Cp'_2LnCH(TMS)_2$, Cp' = η^5-Me_5C_5, Ln = La, Sm, Y, Lu; TMS = Me_3Si; **188a**, R = H; **188b**, R = Me.

pounds **182**–**184** (Schemes 74, 75). Walsh et al. [90] showed that bis-amide zirconium complexes are capable of catalyzing hydroamination of allene with amines. The reaction of allene with 2,6-dimethylaniline in the presence of zirconium complexes followed unusual pattern: instead of expected *N*-isopropenyl-2,6-dimethylaniline (**185b**), *N*-isopropylidene-2,6-dimethylaniline (**185a**) was obtained

Scheme 79.



189a–189c **190a**, **190b** **192** **191a–191f**

189, R = Me (**a**), C_6H_{13} (**b**), Me_3Si (**c**); **190**, R′ = $PhCH_2$ (**a**), CH_2CHCH_2 (**b**); **191**, R′ = $PhCH_2$, R = Me (**a**, 70%), C_6H_{13} (**b**, 40%), Me_3Si (**c**, 50%); R′ = CH_2CHCH_2, R = Me (**d**, 46%), C_6H_{13} (**e**, 30%), Me_3Si (**f**, 41%).

(Scheme 76). The product structure indicated that the reaction occurred at the C=C bond with subsequent hydride shift.

Aryl-substituted allenes were also found [92] to react with N–H compounds in the presence of palladium- and palladium-and-iron-containing catalysts. The most efficient was two-component catalytic system $Pd(dba)_3 \cdot CHCl_3$–dppf [where dba stands for dibenzylideneacetone, and dppf stands for 1,1′-bis(diphenylphosphino)ferrocene]. This system ensured up to quantitative yield of compounds **186a**–**186h** provided that trifluoroacetic acid was added as promotor (Scheme 77).

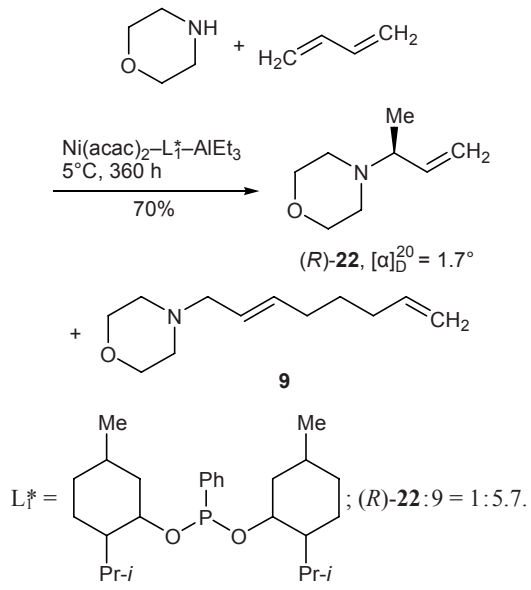
Intramolecular hydroamination–cyclization of amino-substituted allenes was reported in [93]. The reaction was catalyzed by lanthanum, samarium, yttrium, and lutetium complexes. Depending on the number of methylene units separating the amino group from the C=C=C fragment, pyrrolidine (**187**) or piperidine structure (**188**, **189**) was formed (Scheme 78). Hydroamination of conjugated enynes **189a**–**189c** with amines **190a**–**190c** afforded difficultly accessible 1,4-diamines **191a**–**191c** [94] (Scheme 79). Obviously, enyne molecule undergoes double hydroamination, and the authors presumed [94] intermediate formation of aminoallene **192**; however, they failed to isolate and characterize the latter.

10. ASYMMETRIC HYDROAMINATION

As follows from the structure of *N*-(but-1-en-3-yl)-amines **22**, **31**, and **40** and *N*-(octa-1,7-dien-3-yl)-amines **29**, **33**, and **43**, hydroamination of 1,3-dienes is accompanied by appearance of a chiral center; therefore, these reactions can be used to achieve asymmetric induction. In 1975 we were among the first to report on enantioselective hydroamination of butadiene with morpholine [95] (Scheme 80).

Enantiodifferentiation observed in [96] originated from the presence of phenyldi(menth-3-yloxy)phosphine (L_1^*) as chiral ligand in the catalyst. Replacement of L_1^* in the nickel-containing catalyst by tris(menth-3-yl) phosphite (L_2^*) made it possible to synthesize optically active amines (*R*)-**22** and (*R*)-**29** with an ee (enantiomeric excess) value of ~78%, the chemical yield being ~30% (Scheme 81). Further increase in the optical yield of 1,3-diene hydroamination products was achieved using palladium catalyst activated by Trost chiral ligand (L_1^*) [97] (Scheme 82). The optical purity of (1*R*)-*N*-phenylcyclohex-2-en-1-amine (*R*)-**56** was about 95%.

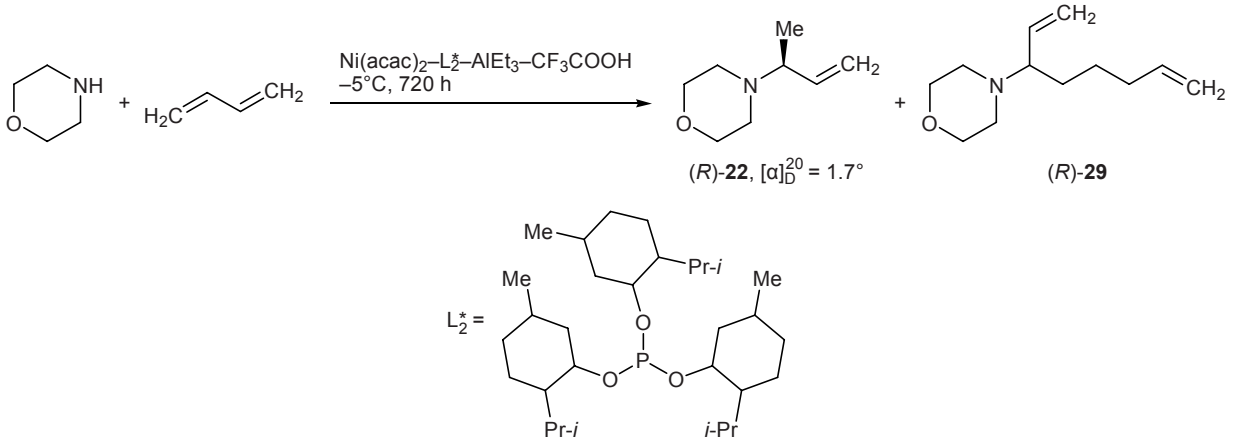
Scheme 80.



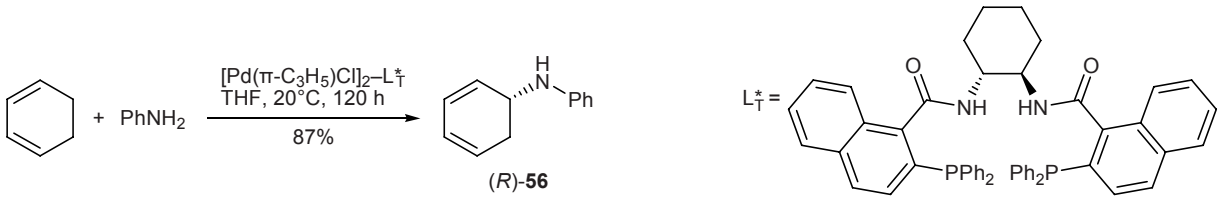
Presumably, hydroamination of 1,3-dienes with 100% optical yield is difficult to accomplish. In any case, such conclusion can be drawn from the data of [62], according to which optically pure (1*R*)-*N*-phenylcyclohex-2-en-1-amine (*R*)-**56** undergoes racemization in the presence of chiral catalyst $[(\pi\text{-}C_3H_5)PdCl]_2$–$L_1^*$ used in [61] in the hydroamination of cyclohexa-1,3-diene with aniline (Scheme 83).

A necessary condition for racemization of (*R*)-**56** is the presence of free amine or trifluoroacetic acid in the system. The reason for the observed unusual catalytic effect is the ability of palladium (as well as of nickel) complexes to promote allylic shift of tertiary hydrogen

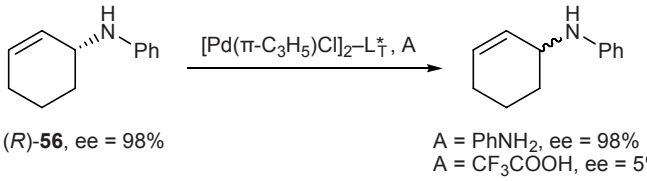
Scheme 81.



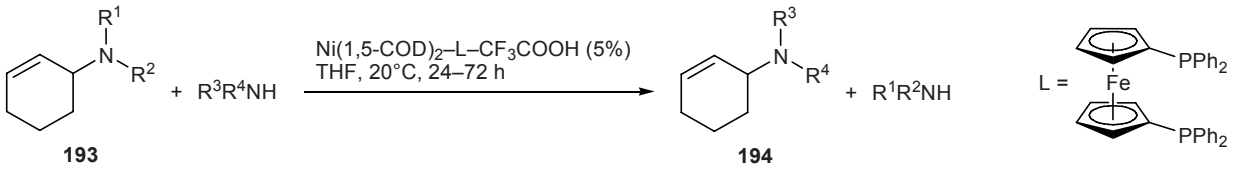
Scheme 82.



Scheme 83.



Scheme 84.



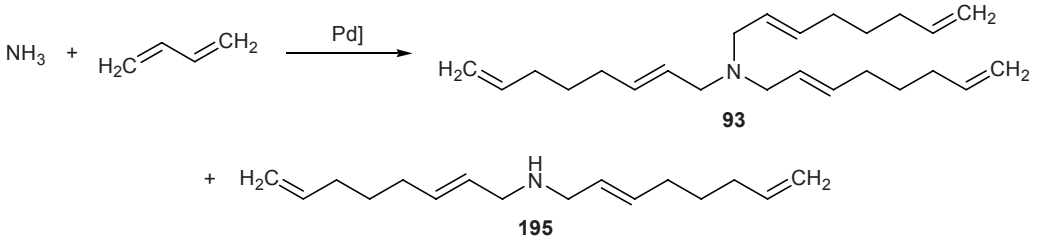
atom, which leads to racemization of optically active allylamines, or amino group exchange through π-allyl complexes, as shown in Scheme 84 for amines **193** and **194** [97].

11. HYDROAMINATION OF 1,3-DIENES WITH AMMONIA AND AMMONIUM SALTS DERIVED FROM MINERAL ACIDS

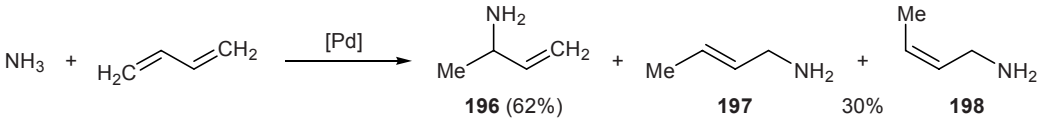
Catalytic hydroamination of 1,3-dienes with ammonia opens synthetic routes to primary, secondary, and tertiary amines with the use of accessible starting materials. The hydroamination of butadiene with ammonia was reported for the first time in 1971 [98]. The reaction was catalyzed by palladium complexes; it occurred under mild conditions (80°C) and afforded a mixture of bis(octa-2,7-dien-1-yl)amine (**195**) and tris(octa-2,7-dien-1-yl)amine (**93**) at a ratio of 24 : 1 (Scheme 85). Tris(octa-2,7-dien-1-yl)amine (**93**) can readily be reduced to trioctylamine which may be converted into the corresponding *N*-oxide, and the latter is widely used as extractant for noble and rare metals and fatty acids [99, 100].

In early studies, hydroamination of butadiene was performed with gaseous ammonia under pressure whose magnitude (15–60 atm) depended on the reac-

Scheme 85.



Scheme 86.



[Pd] = $Pd(OAc)_2$–$(PhPCH_2)_2$; EtOH, 100–145°C, 1 h; conversion of butadiene 90%.

tant ratio, as well as on the nature of inert solvent, ammonia concentration, and temperature [98, 101–105]. Later on, water-resistant palladium catalysts were proposed, and they allowed hydroamination of butadiene to be performed using aqueous ammonia. In this case, the pressure in the reactor was determined mainly by partial butadiene pressure, and it did not exceed 6 atm. Although the use of aqueous ammonia considerably simplified the experimental technology, some new problems appeared. The main of these was sharp reduction of the conversion and overall yield of unsaturated amines (down to 21%). Simultaneously, the selectivity for tris(octa-2,7-dien-1-yl)amine (**93**) decreased, while the fraction of primary octadienylamines increased. Adducts **196**–**198** (1 : 1) were the major products in the reaction of butadiene with ammonia in the presence of 1,2-bis(diphenylphosphino)ethane as activating organophosphorus ligand [104] (Scheme 86).

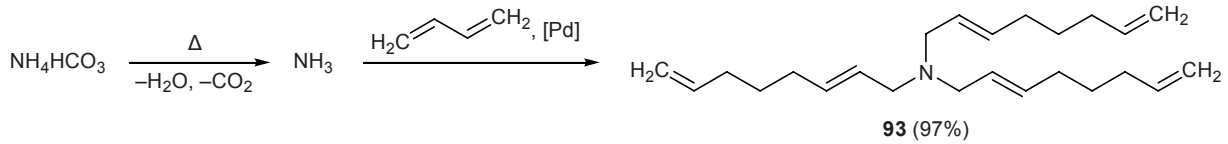
The conversion of NH_3 and butadiene and the yield of unsaturated amines were increased using as catalyst palladium complex activated by water-soluble organophosphorus ligand $P(2\text{-}MeC_6H_3SO_3Na\text{-}4)_3$. The catalytic system $Pd(OAc)_2$–$P(2\text{-}CH_3C_6H_3SO_3Na\text{-}4)_3$ (1 : 4) [106] turned out to be sufficiently effective in the hydroamination of butadiene with aqueous ammonia in pentane (toluene)–water (1 : 1.6) (80°C, 1.5 h). The reaction gave a mixture of octa-2,7-dien-1-amine (**165**) and octa-2,7-dien-3-amine (**166**) with an overall yield of 55–61%, while the yield of tris(octa-2,7-dien-1-yl)amine (**93**) did not exceed 3–8% [107–110]. During the process, the catalytic complex consisting of water-soluble $Pd(OAc)_2$ and $P(2\text{-}CH_3C_6H_3SO_3Na\text{-}4)_3$ resides in the aqueous phase, while the products accumulate in the organic phase. The phases can readily be separated after reaction completion. It is very important that the catalyst in the aqueous phase retains its high activity, and it may be reused up to 10 times [107].

Thus problems related to difficult accessibility and high cost of water-soluble organophosphorus ligand (it is prepared by sulfonation of triphenylphosphine with oleum over a period of 3 days) are partially compensated by the possibility for its repeated use [106–110]. Presumably, the best catalysts for selective synthesis of tris(octa-2,7-dien-1-yl)amine (**93**) via reaction of butadiene with aqueous ammonia are water soluble palladium(II) complexes with sulfoxides, such as $PdCl_2 \cdot 2DMSO$ and $PdCl_2 \cdot n(PSO)$ (where PSO stands for petroleum sulfoxides) [111]. The yield of **93** was 95% in the presence of these catalysts (80°C, 5 h).

It is known that ammonium salts are unstable compounds; they readily decompose with liberation of free ammonia even on slight heating. Decomposition of the following ammonium salts was used in [112] to generate ammonia for subsequent hydroamination of butadiene: $(NH_4)_2SO_4$, NH_4Br, $(NH_4)_2HPO_4$, $(NH_4)_2CO_3$, and NH_4HCO_3. The best source of ammonia was ammonium hydrogen carbonate which decomposed into NH_3, CO_2, and H_2O on heating to 40–60°C. Replacement of ammonia by ammonium salt changed the reaction selectivity. For example, the reaction of NH_4HCO_3 with butadiene in the presence of $Pd(acac)_2$–PPh_3–$AlEt_3$–CF_3COOH gave tris(octa-2,7-dien-1-yl)amine (**93**) in almost quantitative yield [112] (Scheme 87). Carbon dioxide liberated during the process acts simultaneously as activator, thus increasing the selectivity and the yield of tertiary amine **93**.

It is known that urotropin decomposes completely to form formaldehyde and ammonia by the action of

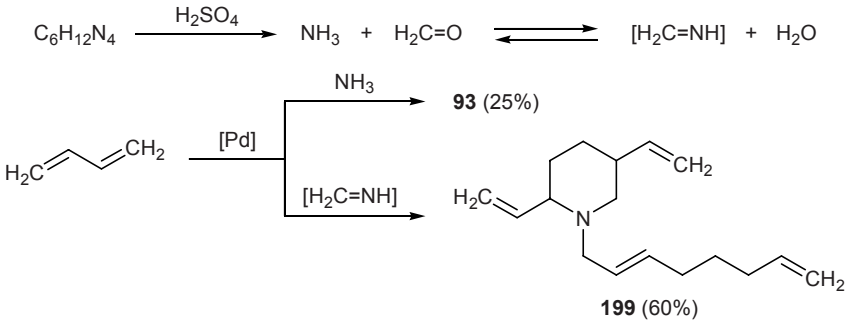
Scheme 87.



93 (97%)

[Pd] = $Pd(acac)_2$–PPh_3–$AlEt_3$–CF_3COOH; water–dioxane, 100°C, 8 h.

Scheme 88.



[Pd] = $Pd(acac)_2$–PPh_3–$AlEt_3$–H_2SO_4, 1 : 3 : 2 : 1.5; water–toluene, 100°C, 6 h.

strong acids; therefore, urotropin can be used as synthetic equivalent of ammonia. In the reaction of butadiene with urotropin in acid medium (i.e., under conditions favoring its decomposition) in the presence of $Pd(acac)_2$–PPh_3–$AlEt_3$ tris(octa-2,7-dien-1-yl)amine (**93**) was obtained in 25% yield, whereas the major product was 2,5-divinyl-1-(octa-2,7-dien-1-yl)piperidine (**199**). The formation of the latter was rationalized [113] by generation of methylenimine from formaldehyde and ammonia (Scheme 88).

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